TRANSACTIONS

of the
American Society for Steel Treating

CONTENTS

The object of the Society shall be to promote the arts and sciences connected with either the manufacture or treatment of metals, or both.—Constitution A. S. S. T., Art. II.

FACTORS AFFECTING THE INHERENT HARDEN-ABILITY OF STEEL

By Edgar Collins Bain

Abstract

The hardenability of a steel depends upon the actual rate at which its austenite transforms to fine pearlite at the particular temperature at which this reaction sets in most promptly. The precise temperature at which this transformation rate is greatest depends upon the composition of the steel; in any case, it is this maximum rate at temperatures near 950 degrees Fahr. (500 degrees Cent.), which determines the critical quenching speed which must be exceeded if the steel is to be hardened.

This maximum rate of austenite transformation to products other than martensite is in turn largely determined by the condition of the austenite at the moment of quenching with respect to two factors:

(1) its composition with respect to dissolved elements, most of which retard, though some may hasten, its transformation to pearlite. Manganese, chromium, nickel, silicon, and aluminum definitely retard the reaction and so contribute directly to deep hardening about in the order named; on the other hand, tungsten, cobalt, molybdenum, vanadium, and possibly oxygen appear to induce shallow hardening, though most probably indirectly by restricting grain growth.

(2) its effective grain size. The finer the grain, the more rapid is the transformation to fine pearlite, and correspondingly the lower is the hardenability. Effective grain size seems to be the most potent single factor influencing hardenability; it in turn is probably controlled largely, for any specified temperature, by the obstruction to grain growth offered by large numbers of very finely dispersed particles, of exceedingly small aggregate mass, comprised presumably of stable oxides such as alumina, vanadia, and probably silica or silicates.

THE affection and respect surrounding the memory of Edward De Mille Campbell have not diminished with the passing of the seven years since his death in September 1925. This society has

fittingly set apart an hour each year at the Annual Meeting in honor of this outstanding scientist and educator. On all these occasions we have heard brilliant discourses upon subjects related to the work of Professor Campbell.

In expressing my deep appreciation of the high honor conferred upon me as the seventh Campbell Memorial Lecturer, it is my pleasant duty to acknowledge the rightful share of my associates in this distinction. I would particularly mention E. S. Davenport who has contributed so greatly to the work of our laboratory. I am indebted likewise to E. L. Roff, J. R. Anderson, Gustav Guillich, J. J. B. Rutherford, and W. S. N. Waring. And finally it is with the greatest sense of gratitude that I refer to Dr. John Johnston, Director of Research and Technology, United States Steel Corporation, under whose encouragement and sympathetic counsel the studies to be reported today have been made.

INTRODUCTION

In this inquiry into the hardenability of steel we refer to the property which reflects itself in the depth to which the steel may be hardened when quenched from a suitable temperature into a medium of sufficient heat-withdrawing power to develop martensitic hardness over the surface of the piece. Quite clearly, this complex property relates only to nonaustenitic steels of sufficient carbon content to yield a hard martensite, and in the present discussion we shall not refer to the hardening of any steels carrying less than half of one per cent of carbon. To define the subject further, let us assume that cylinders of equal size, say one inch in diameter, are prepared from a wide variety of carbon and low alloy steels of similar carbon content, and that these cylinders are then similarly heated and quenched. Upon examining the fractured sections, we shall discover that the steels may vary greatly as to hardening characteristics. Some will have hardened through and through, while, at the other extreme, perhaps only a thin surface layer will have hardened, and even this hard surface may be discontinuous, with soft spots extending through in some areas. Some writers have appropriately designated the undifferentiated controlling factors which account for this variation as the "hardening power" of steel; others have spoken of "hardenability." Either designation is unequivocal and, it is believed, both call to mind an accurate image of the behavior, although perhaps the second term, "hardenability," is prefer-

able. The quenching bath, one might say, is endowed with hardening power, but the steel possesses its degree of hardenability. In Fig. 1 are shown a series of sections through such cylinders as were postulated; they reveal, from 1 to 8, a continuously increasing depth of hardness, although the carbon content varies little from one to
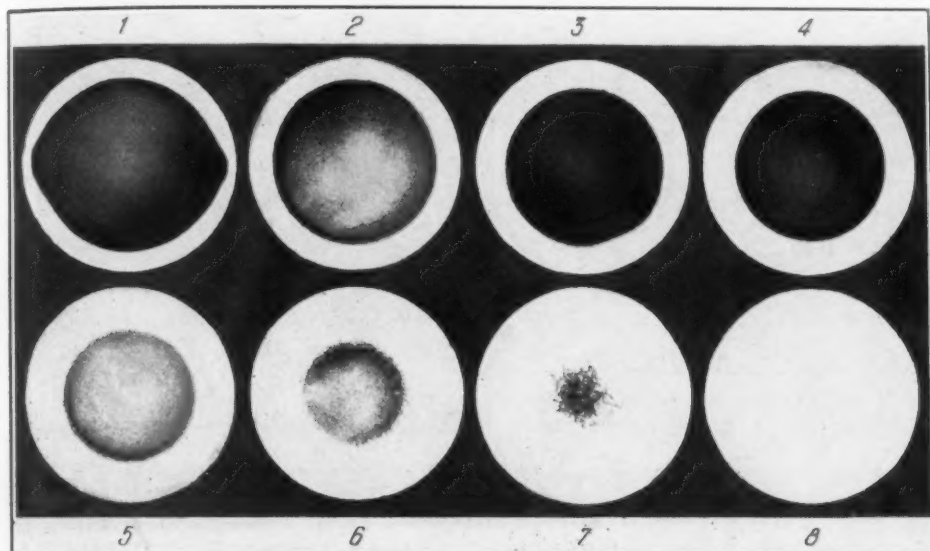
Fig. 1—Sections of Hardened One-inch Rounds of 1.0 Per Cent Carbon Steels of Different Hardenability.

another and none contains as much as one per cent of total alloying elements. For this purpose a middle section across the cylinder has been ground flat, then polished and etched to darken that portion of the steel which has not developed the hard martensite structure. This procedure suffices to estimate the relative hardenability of the steels. If a more precise determination of the hardening tendencies is required, an exploration of the hardness may be made, for example, with the Rockwell hardness tester and the values of hardness across a diameter plotted with reference to location. Fig. 2 shows the hardness distribution across the several specimens just observed in the etched condition. It will be seen that they fall in a similar series. To secure such a range of hardness penetration with the steels employed it was necessary to vary some of the factors which are to be discussed.

In attempting to differentiate among the factors affecting the hardenability of steel, it is convenient to classify them according to whether they are inherent in the steel or developed in a particular
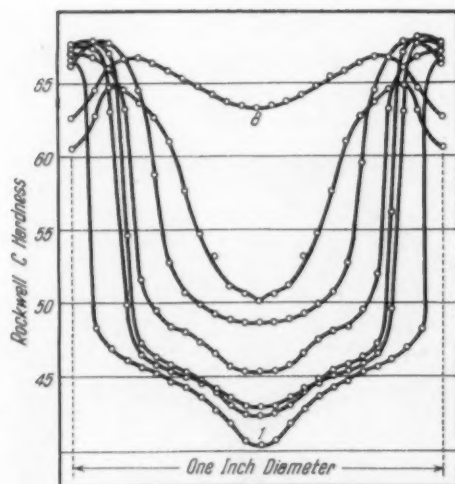
Fig. 2—The Hardness Across the Diameter of the Sections of Fig. 1.
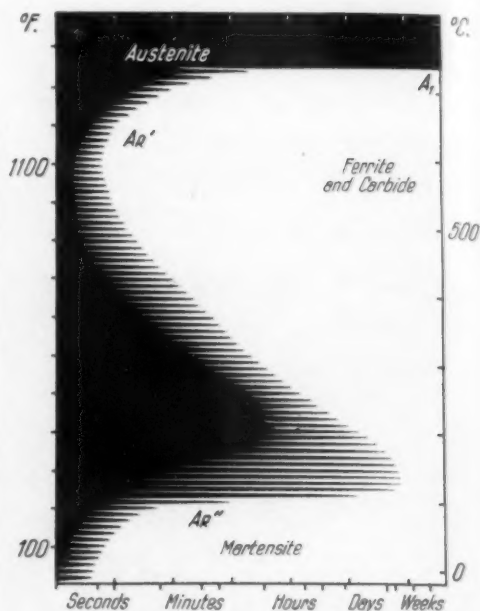
Fig. 3—Relative Time for Austenite (Black) Transformation to Ferrite and Carbide (White) at Various Temperatures. Logarithmic Abscissa.

steel specimen during its preparation for the quenching. In building up a concept of the nature of hardenability we have found one viewpoint very useful. It appears that hardenability is uniquely correlated with at least one observed behavior of steel. To quote from a previous paper[1]—

"The reaction (austenite to ferrite and carbide) proceeds with maximum rapidity in the general vicinity of 1100 to 930 degrees Fahr. (600 to 500 degrees Cent.) and in that temperature range a few seconds (at most) suffice to permit the austenite to transform to the nodular fine-pearlite type of ferrite-carbide association. It becomes apparent that in hardening steel the sole task of a commercial quenching medium is to abstract heat from the steel with rapidity sufficient to prevent this rapid reaction, and to cool the austenite unchanged through this temperature zone into a temperature range (below about 300 degrees Fahr., 150 degrees Cent.) wherein the harder constituents are formed. Similarly it became apparent that the real function of alloying elements which induce deep hardening is merely that of slowing up the reaction in this temperature range of maximum rapidity, namely the 1100 to 930 degrees Fahr. (600 to 500 degrees Cent.) zone."

Fig. 3 shows schematically the time-lag and transformation time,

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[1]Henry Marion Howe Memorial Lecture, 1932, Edgar C. Bain, "On the Rates of Reactions in Solid Steel," *Transactions*, American Institute of Mining and Metallurgical Engineers, 1932, Vol. 100, Iron and Steel Division, p. 13-46.

(abscissa on logarithmic scale) for austenite (black) to undergo transformation to ferrite and carbide (white) at various constant temperatures to which a hypereutectoid steel has been undercooled. Such explorations on several steels have been published by E. S. Davenport. This diagram assumes that minute specimens of fully austenitic steel were almost instantly brought down to the various temperatures, there to transform under observation at constant temperature. These conditions are not those of steels quenched into baths at ordinary temperatures below 200 degrees Fahr. (100 degrees Cent.), but it is easy to infer that such a steel as is set forth in the diagram must be cooled through the Ar′ range at a velocity somewhere in the vicinity of 180 degrees Fahr. (100 degrees Cent.) per second, if it is to escape some transformation to nodular fine pearlite and instead to form martensite in the Ar″ region. No time-temperature cooling curve for a moderate size piece of steel quenched into a room-temperature aqueous bath could ever be first so steep and then so flat as to transgress the line of initial action between about 900 and 400 degrees Fahr. (500 and 200 degrees Cent.), and hence, under the ordinary quenching conditions, no troostitic structures, such as may be developed by constant temperature transformation, are to be found. This statement appears the more reasonable when it is considered that the chart of Fig. 3 would extend some 20 miles in horizontal direction, if it were plotted on the ordinary linear abscissa of time at the same scale as chosen for the first second of lapsed time.

Now, a time-temperature chart of the beginning of transformation may be constructed which applies to various cooling rates instead of various constant temperatures. For clearly the slowly cooled steel actually transforms at a higher temperature than the rapidly cooled. Such a chart will apply to zones in larger masses of steel quenched with different degrees of severity. The quenching or cooling media being at a temperature below Ar″ will in any event abstract heat continuously until the metal itself is essentially at the bath temperature regardless of the transformation temperature. The chart will show only how the temperature at which transformation begins depends upon the rate of the heat abstraction. One characteristic of this chart must certainly be the discontinuity in the graph indicating the time and temperature of initial transformation, between about 900 and 300 degrees Fahr. (480 and 150 degrees Cent.). Fig. 4 shows schematically this sort

of diagram for a normal eutectoid carbon steel, and superimposed upon it are four typical cooling curves for some part of a steel mass cooled to the recalescence point at different rates. The unfamiliarity of the shape of these cooling curves is a matter of the logarithmic time scale. In a slowly cooled steel specimen (as in the furnace) a
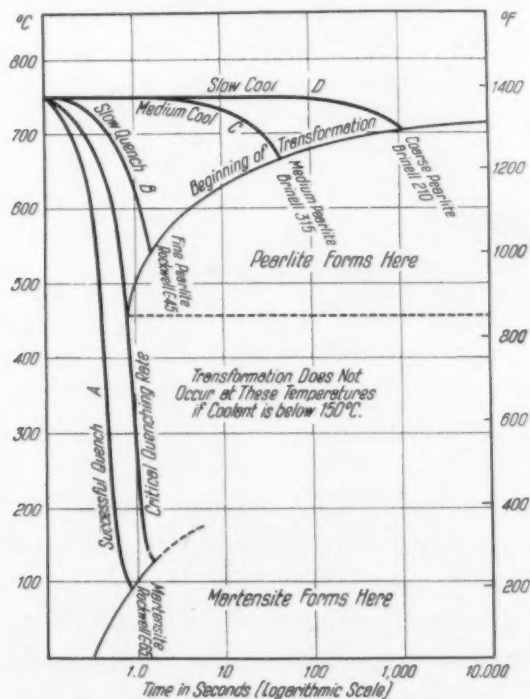
Fig. 4—Chart Showing Schematically the Time and Temperature of Initial Transformation of a Eutectoid Steel as Cooled at Various Uniform Rates. Logarithmic Abscissa.

zone whose cooling rate conformed with curve D began to transform to coarse pearlite at 1300 degrees Fahr. (705 degrees Cent.), and possessed a hardness of about 210 Brinell. A less slowly cooled austenite zone (as in free air) inaugurated transformation at 1215 degrees Fahr. (656 degrees Cent.), but to a pearlite of finer lamellae with a Brinell hardness of about 315. This cooling rate corresponds to curve C, about 50 times as rapid as for curve D. Turning to the more rapid abstraction of heat by quenching, we may find within one specimen of steel a zone cooling in accord with curve A, and a zone cooling as in curve B. Since the thermal conductivity of steel is not infinite, the interior, remote from the coolant, must, at any instant, be hotter and therefore be cooling less rapidly than the surface. The zone at and near the surface may cool in accord with

curve A and miss the formation of any fine pearlite, while metal at some interior zone will encounter the Ar′ transformation as in curve B, and therefore not become wholly martensitic. The minimum cooling rate which will just prevent the transformation at the higher temperature is designated the "critical cooling rate" and is shown in
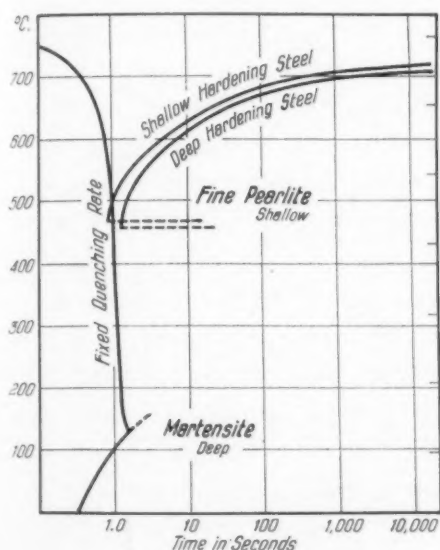
Fig. 5—Chart Showing Schematically the Significance of Two Transformation Rates upon Hardening Depth. Logarithmic Abscissa.
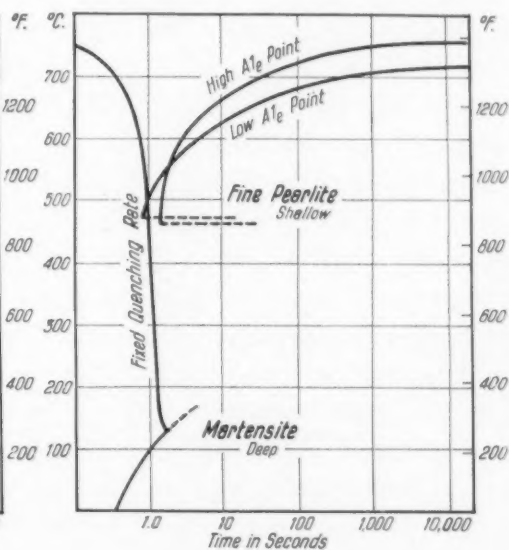
Fig. 6—Chart Showing Comparison Between Transformation Characteristics of a Shallow Hardening Steel of Low Critical Temperature and a Deep Hardening Steel of High Critical Temperature. Logarithmic Abscissa.

the chart between curves A and B. This particular rate of heat abstraction will generally be marked by the inner zone of the martensitic rim of the specimen.

By this time it will be clear that the rate at which austenite prepares to transform at the 1100-900 degrees Fahr. (600-500 degrees Cent.) range of maximum activity controls the hardenability of a steel. For the sake of brevity we speak of transformation rate, or reaction rate, but the interest centers particularly in the time interval of nucleation, prior, really, to measurable reaction. In Fig. 5 are shown the time-temperature plots for initial transformation in two steel specimens which possess different rates of reaction in the important range. An increase in manganese content could easily shift the curve in this manner. It will be seen that a particular zone in similar specimens of the two steels would in the one case be fully hardened and in the other case remain soft when quenched in a

medium capable of cooling the metal in accord with the one cooling curve as drawn.

From the simple geometry of the chart of Fig. 5, it may be seen that steels of lower true critical point $(A1_e)$ will, in general, have lower rates of reaction and therefore tend to transform at lower temperature and to form harder constituents than steels of higher critical point. This must be true if for no other reason than that steels of higher $A1_e$ point, when quenched in a given manner, are cooling for a greater period of time within the temperature range wherein transformation is possible, i.e., wherein the steel is actually preparing to transform. Nevertheless, it is still possible that the interval of minimum time-lag may actually be shorter for the steel of lower critical point. This condition would be illustrated by the comparison curves in Fig. 6. Here the curves marking the beginning of transformation on cooling actually cross, the steel of rapid transformation rate at 1300 degrees Fahr. (705 degrees Cent.) being the deep hardening steel when quenched at a rate near the critical rate. We shall later find an example of an alloying element, which, when added to steel, will induce this unexpected behavior.

A grain of austenite in transforming soon develops a high rate of reaction, even though it lags at first; but as soon as about a third of the grain is transformed the velocity of reaction falls off rapidly and for this reason it is possible to find in the intermediate layers of a quenched bar of steel many of the original grains of austenite, which are partly martensitic and partly fine-pearlitic.

On this basis hardenability of steels is not a matter of static properties, but rather is concerned solely with rates.

THE FACTORS INVOLVED IN HARDENABILITY

Before turning attention to the factors in the inherent hardenability, one can perhaps dispose of certain superficial inequalities among steels which obviously would very seriously confuse experimentation on inherent rate effects. These may be termed external factors.

I.   Factors External to the Steel

Quenching Temperature—With all other conditions remaining unaltered in the homogeneous austenite ready for the quench, the transformation rate at any constant temperature will be entirely independent of the temperature from which the austenite is suddenly

quenched, but the rate of cooling in any quenching medium will vary with the temperature of the piece at the moment of introduction into the bath. The rate is roughly proportional to the temperature difference between steel and bath, and, as a result, the time required for any small portion of the quenched piece to pass through the important temperature zone is the less the higher the quenching temperature. This influence of high quenching temper-
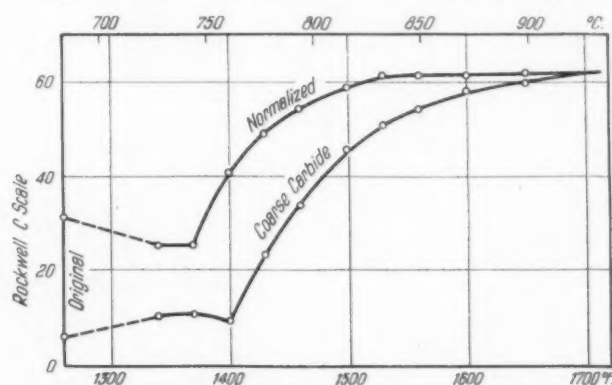
Fig. 7—Comparison of the Hardness of a Normalized and a Coarsely Spheroidized Steel of Same Analysis After a Brief Heating at Various Temperatures Prior to Quench.

ature is, of course, relatively slight in comparison with the structural changes which high heating temperature may induce, but it is of sufficient importance, nevertheless, to require close control. In the studies reported here, when a high temperature heating was required in one specimen of a comparative series, it was not quenched therefrom but first cooled to the standard temperature.

Structure Prior to Heating—Let us consider two bars of the same steel; the one is a normalized bar with a fine pearlitic or troostitic structure, the other contains large carbide particles coarsely spheroidized. If specimens from both bars are now briefly heated and quenched, we may find the normalized specimen fully hardened and the other not hardened even on the surface. The cause of this disparity in hardenability must lie in the constitution of the austenite responsible for the hardening. The large carbide particles are only slowly dissolved upon heating, while short paths of diffusion permit the rapid solution of carbon from the fine dispersion of the normalized steel. Such a comparison is shown in Fig. 7. In the one case an austenite was quenched which was largely a low carbon solid solution of little hardening capacity, not representative of the steel, but rather of its misuse. When heated

sufficiently long or to sufficiently high temperatures prior to quench-ing, so that the austenite is substantially homogeneous, the two bars harden precisely alike. This effect of unlike annealed structures may persist even after no undissolved carbide particles remain in the steel about to be quenched. If the austenitic metal in the microscopic zone formerly occupied by a carbide particle is saturated in carbon
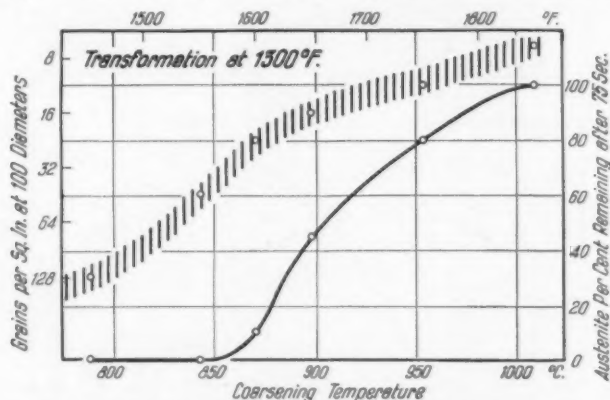
Fig. 8—Proportion of Austenite Still Untransformed After 75 Seconds at 1300 Degrees Fahr. (705 Degrees Cent.) Following Quenching Thereto From Various Tem-peratures. The Grain Size Developed is Shown by Ruled Band.

and the austenite most remote therefrom has acquired, by diffusion, only a few tenths of a per cent of carbon, it clearly transforms more rapidly on the average than does the homogeneous austenite of the same mean composition. As a result of such variations which relate only to the history, and therefore the structure of the particular specimens employed, it has been necessary in our studies to provide for the substantial homogenization of the austenite under examina-tion for hardenability.

Influence of the Developed Austenitic Grain-size—It will be recalled that a fine austenitic grain size was a very usual accompani-ment to the carburized steel described by McQuaid and Ehn[2] as hardening unsatisfactorily, i.e., with soft spots. It occurred to us that fine grain size may be a possible cause, rather than a mere symptom, of the rapid transformation rate responsible for low hard-ening capacity. (By "grain-size" will always be meant the austenite grain size prior to quench). This hypothesis was tested as to valid-ity. By heating a steel to successively higher temperatures a larger and larger grain size may be established in the homogeneous aus-

[2]H. W. McQuaid and E. W. Ehn, "Effect of Quality of Steel on Case-carburizing Results," *Transactions*, American Institute of Mining and Metallurgical Enginers, 1922, Vol. 67, p. 341-91.
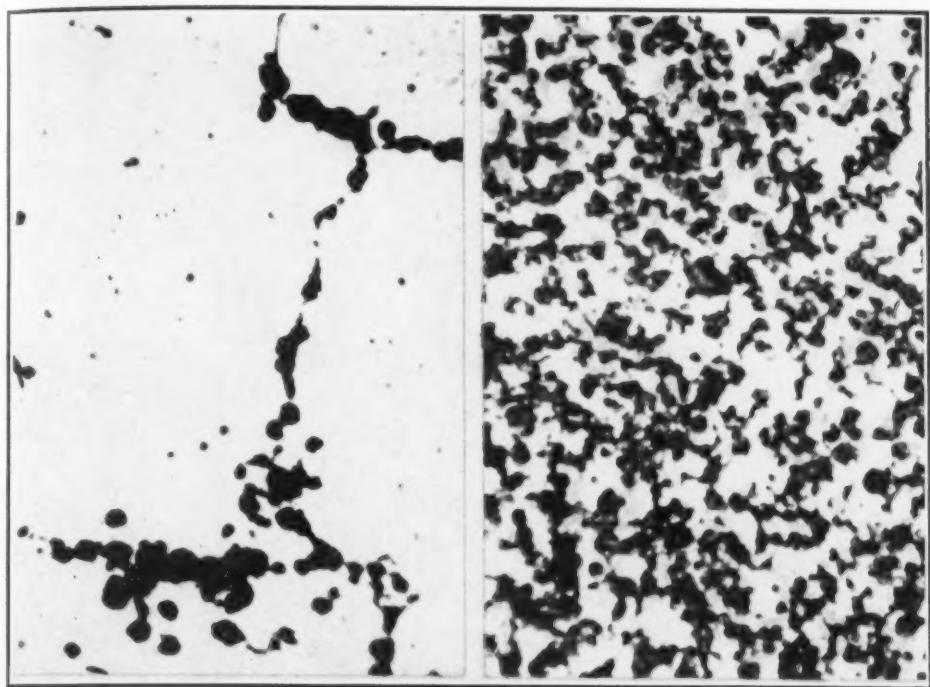
Fig. 9—Photomicrographs, at × 100, Showing the Relative Proportions of Martensite and Nodular Fine Pearlite in the Semihardened Zone of Similar Specimens of the Same Steel, the One Coarsened, the Other of Fine Austenite Grain.

tenite. The rate of transformation in the fine pearlite, i.e., Ar′, temperature range might be determined for the different grain sizes developed, but, since we are not considering different steels, the relative rates may be determined at a higher temperature, where accuracy in estimation is possible. Fig. 8 shows the proportion of the homogeneous austenite (solid line) which still remains after 75 seconds at 1300 degrees Fahr. (705 degrees Cent.) in minute specimens differing only in grain size (shown in ruled band). The variation in reaction rate is clearly a function of the coarsening temperature employed, and hence, of grain size. This is further illustrated by the two photomicrographs of Fig. 9, showing the same steel in coarse and in fine grain size as quenched just under the critical rate. It will be observed that while the fine pearlite nodules themselves are of essentially the same size, their number, and hence total volume, is much greater in the fine-grained specimen. The two etched sections of Fig. 10, with the accompanying hardness plot, show the direct effect of grain size upon depth of hardening. The deeply hardened specimen was coarsened at 1800 degrees Fahr. (980 degrees Cent.), the shallow at 1550 degrees Fahr. (845 degrees Cent.),

but both were identically quenched from a temperature just below A$_{cm}$, 1375 degrees Fahr. (745 degrees Cent.). The actual grain size contrast was as follows: for the coarsened specimen an average of 16 grains per square inch at 100 diameters (No. 5) and for the fine-grained specimen about 150 grains per square inch (finer than
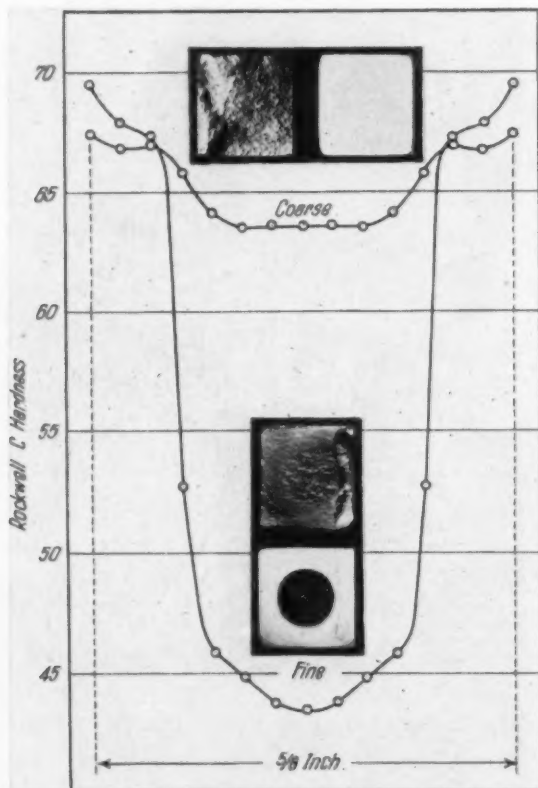
Fig. 10—Depth of Hardening as Affected by Coarsening Treatment. The Specimen Hardened Throughout was Coarsened at 1800 Degrees Fahr. (1000 Degrees Cent.), the Other at 1550 Degrees Fahr. (845 Degrees Cent.); Both Quenched from 1375 Degrees Fahr. (745 Degrees Cent.).

No. 8). To secure a homogeneous austenite, they were both first prequenched from a high temperature to establish a fine carbide dispersion and to insure rapid carbide solution in the heating. That a steel during coarsening is not modified in other respects apart from its grain size may be inferred from its second response to coarsening. Fig. 11 shows the ordinary cooling curves for the two specimens, equalized as to temperature at 1700 degrees Fahr. (925 degrees Cent.), after one had been coarsened. The coarsened specimen has the lower recalescence point characteristic of a deeper hard-

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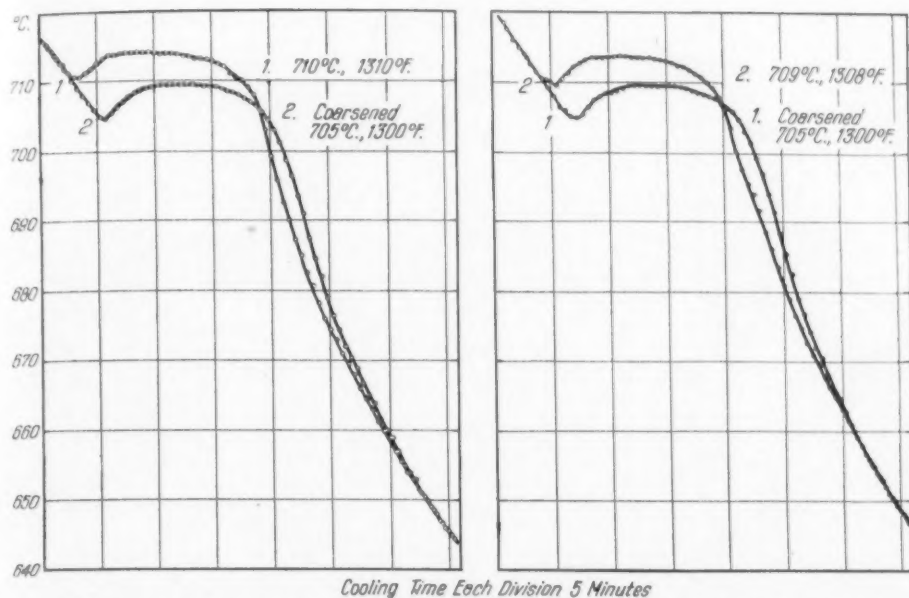
Fig. 11—Simultaneous Cooling Curves for a Eutectoid Steel, One Specimen Coarsened, the Other of Natural Grain Size. The Specimens were Reversed in the Second Chart.

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ening steel. The same specimens were again compared but reversed. The finer grained specimen received the coarsening treatment. Substantially the same effect of grain size is shown, indicating that no permanent effect is imparted to the steel by a grain size inheritance or otherwise. The microstructure shows no difference between the first comparison and the second reversed comparison. It may be concluded that grain size in the austenite, prior to transformation, so affects the transformation characteristics of the steel as a whole that coarse-grained steel is essentially a deep hardening steel of slow reaction characteristics, while fine-grained steel is a shallow hardening steel of high reaction speed. The photomicrograph of Fig. 12 shows the structure of a hypereutectoid steel previously coarsened at 2000 degrees Fahr. (1095 degrees Cent.), after it transformed naturally on cooling at 1297 degrees Fahr. (703 degrees Cent.), while Fig. 13 shows the microstructure of the uncoarsened steel, identically cooled, which transformed at 1305 degrees Fahr. (707 degrees Cent.). We shall later have occasion to refer to this marked difference in structure, which is certainly not unlike the "normal" and "abnormal" distinction of the McQuaid-Ehn test.

II.   The Inherent Hardenability of Steels

Up to this point we have discussed the influence upon harden-

Fig. 12—Microstructure of a Hypereutectoid Steel as Cooled 4.5 Degrees Fahr. (2.5 Degrees Cent.) per Minute After Coarsening at 2000 Degrees Fahr. (1100 Degrees Cent.). × 1500.

ability exerted by certain structural changes—notably austenite grain size and the annealed carbide-particle size, which, to some extent at least, may be varied at will in any steel. For that purpose, we have, therefore, isolated those factors for study by employing the same or very similar steels for the comparisons. Now it may be predicted with assurance that composition likewise will affect structure by fostering one type in preference to another. For example, it may be found that the major influence of an element is to restrict grain growth in the austenite. Such influences we will term "secondary", reserving the word "primary" for the fundamental contributions of the several elements in simple solid solution in the austenite. The secondary effects may well be of no less significance than the primary. In studying primary composition effects, it will be desirable

Fig. 13—Microstructure of the Steel of Fig. 12 as Cooled 4.5 Degrees Fahr. (2.5 Degrees Cent.) per Minute From 1725 Degrees Fahr. (940 Degrees Cent.). × 1500.

to adjust structure as nearly uniform as possible, but in many cases, unfortunately, uniformity will not be attainable. The secondary effects may obscure the primary. But in some cases it will be quite possible to consider the effect of increments of the alloying element in excess of that amount which exerts its first marked secondary effect upon structure.

The Primary Effects of Alloying Elements upon Hardenability

By means of such devices as were suggested above the direct effect of a number of elements has been approximately evaluated.

Carbon—The hardening capacity of steel clearly increases with increase in the carbon content up to the eutectoid point. There is excellent reason to believe, however, that carbon in excess of this

amount may actually reduce the hardenability of carbon steel when it is wholly in solution in the austenite about to be quenched. One may reason that the velocity of transformation is essentially the same for the austenite of eutectoid composition whether or not it has proeutectoid ferrite or carbide associated with it. But, as has been shown, even below $A1_e$ the proeutectoid phase tends to make its appearance out of austenite ahead of the formation of fine pearlite and
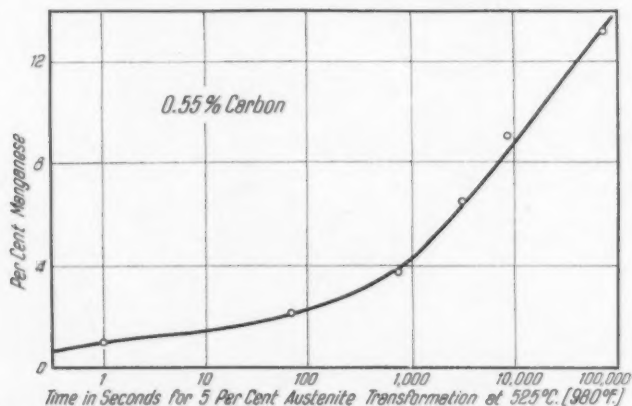
Fig. 14—The Time Required for the First 5 Per Cent of the Homogeneous Austenite to Transform at 980 Degrees Fahr. (525 Degrees Cent.) Plotted as a Function of the Manganese Content in 0.55 Per Cent Carbon Steels.

some heat must thereby be evolved. If so, then the cooling is retarded and the resultant diminished cooling rate for the steel may not be in excess of the critical quenching speed. This would apply if only traces of the proeutectoid constituent were rejected. The frequent occurrence of dark etching fine pearlite associated with martensite in hypereutectoid steel gives this hypothesis some validity.

Manganese—Little need be said of the vigorous influence of manganese to increase depth of hardening. In high carbon steel it may progressively contribute oil hardening properties and finally air hardening properties as it is present to the extent of from 1.5 to 4 or 5 per cent. Manganese, however, promotes the retention of austenite along with martensite in the quenched steel and this condition is not always desirable. Seemingly not all elements of the deep hardening class act so strongly in this respect. The chart of Fig. 14 shows the rapid increase in sluggishness brought about by manganese; the time interval for the formation of the first 5 per cent of fine pearlite at about the temperature of maximum activity is

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Nickel—Similar to manganese in this respect, nickel increases capacity for hardening. Like manganese, it also lowers the true critical points, but it is necessary to employ two or three times as much nickel alone for equal increments in hardening penetration.

Chromium—Chromium alone is somewhat less effective than manganese in increasing the depth of hardening, but even small proportions in conjunction with nickel or manganese appear to increase

Fig. 15—The Rate of Transformation of Austenite at 1320 Degrees Fahr. (715 Degrees Cent.) in Three 0.55 Per Cent Carbon Steels of Indicated Chromium Content.

hardenability very materially. It may be recalled that the austenite of a 13 per cent manganese, 0.50 per cent carbon steel does not transform at all at room temperature, while a 13 per cent chromium steel of the same carbon content produces a reasonably hard martensite. In the Ar′ range the manganese steel begins to transform only after an interval 50 times as long as that for the chromium steel, but Ar′ is fully 350 degrees Fahr. (200 degrees Cent.) higher for the chromium steel. Doubtless large chromium contents are not relatively so effective as small, as is probably the case also with other elements.

Perhaps the most interesting feature of the transformation of the higher chromium steels is that the chrome-bearing austenite is very sluggish in inaugurating transformation, but that the pearlite formation is rapid, once it begins. Fig. 15 illustrates the progress of the reaction in three 0.55 per cent carbon, chromium steels, made to transform at a constant temperature of 1320 degrees Fahr. (715 degrees Cent.). It is generally believed that just below $A1_e$ carbon is more soluble in the ferrite of chromium steels than in the carbon steel ferrite. However that may be, the chromium steels illustrate very well that the property of deep hardening relates to the sluggishness of the beginning of reaction rather than its rate after it is well under way.

At the moment it is difficult to say with assurance whether or not the addition of a few per cent of chromium to a steel of, for example 0.55 per cent carbon, raises or lowers its true critical points; we shall tentatively place it with manganese.

Tungsten—The evidence is rather surprising with respect to tungsten. In moderate additions tungsten clearly decreases the hardening depth of steels; very high additions may have a retarding effect upon the reaction and accomplish deep hardening. In the first
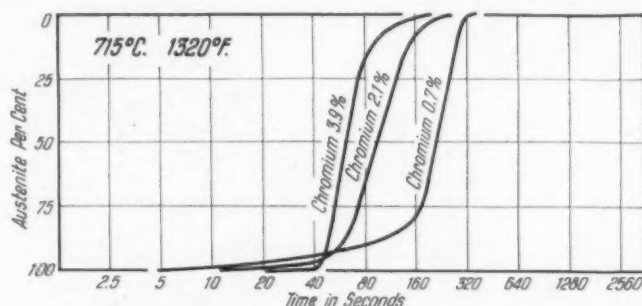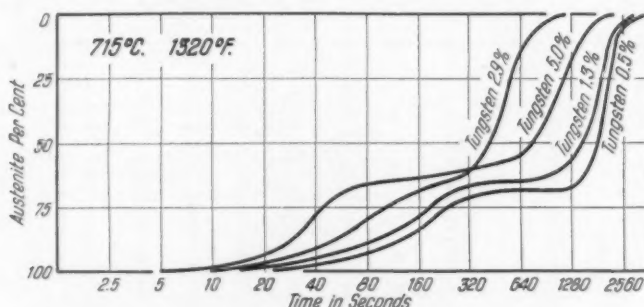

Fig. 16—The Rate of Transformation of Austenite at 1320 Degrees Fahr. (715 Degrees Cent.) in Four 0.55 Per Cent Carbon Steels of Indicated Tungsten Content.

place, it is difficult to develop coarse grain in a 3 or 4 per cent tungsten, 0.55 per cent carbon steel. The fine grain contributes to shallow hardening. Furthermore, the extraordinarily fine nature of the fine pearlite imparts a hardness to the steel which approaches that of martensite—58-60 Rockwell C. One may say perhaps that tungsten inhibits martensite formation but forms a remarkably hard substitute. In tempered steels its shallow hardening effect would certainly not be discovered. Tungsten, likewise, definitely elevates the true critical points in steels. Fig. 16 shows the relative reaction velocities at 1320 degrees Fahr. (715 degrees Cent.) for four tungsten steels with 0.55 per cent carbon. The grain growth tendency falls off rapidly with increase in tungsten content, a point to which we will later have occasion to refer.

Molybdenum—Data are not available on the behavior of molybdenum steels of constant carbon content and with increasing molybdenum. The meager evidence points to a similarity between tungsten and molybdenum. Tentatively molybdenum will be placed in the category with the contributors to shallow hardening or accelerators of reaction rate.

Vanadium—The familiar carbon-vanadium steels are so defi-
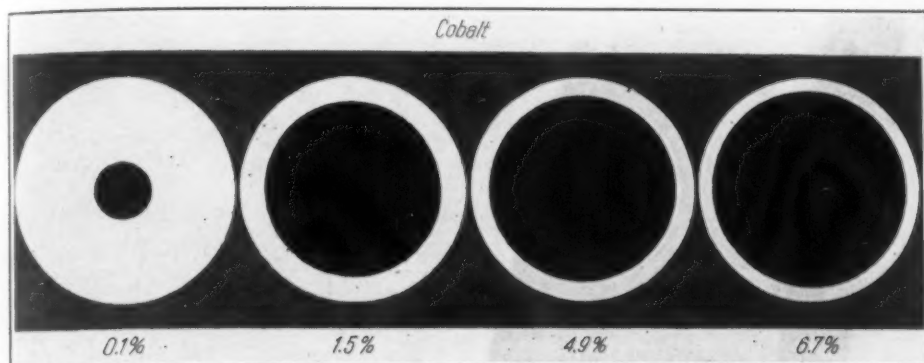
QUENCHED FROM 940 DEGREES CENT. (1725 DEGREES FAHR.)
Fig. 17—Graphic Representation of Depth of Hardening in a Series of 0.90 Per Cent Carbon Steels with Indicated Cobalt Content as Reported by Houdremont.

nitely shallow hardening that vanadium may at once be placed in the class with tungsten, but this may reflect the secondary effect rather than the primary.

Cobalt—In large amount, cobalt is a most extraordinary accelerator of reaction rate. Utterly unlike nickel, in this respect, it produces a steel of shallow hardening characteristics. Some years ago
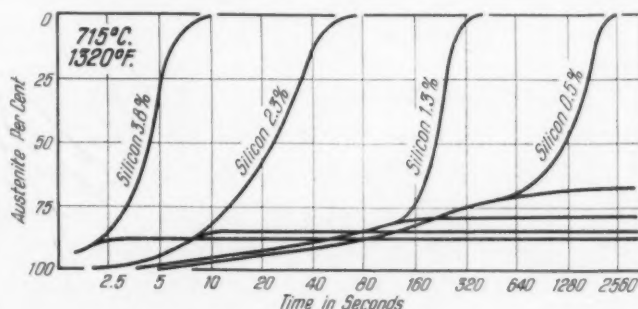
Fig. 18—The Rate of Transformation of Austenite at 1320 Degrees Fahr. (715 Degrees Cent.) in Four 0.55 Per Cent Carbon Steels of Indicated Silicon Content.

your speaker was much disturbed at finding a 15 per cent cobalt, 0.60 per cent carbon steel soft after an oil quench, but positively dismayed when a quench into brine produced only a fine pearlite structure. Houdremont has recently secured quantitative information on the depth of hardening of a series of cobalt steels of two different carbon contents. The results are shown graphically in Fig. 17 for the series containing about 0.9 per cent carbon. Cobalt slightly elevates the critical points of the steels to which it is added. Houdremont shows a consistent and pronounced grain size diminution effect with increasing cobalt content.

Silicon—The constitution-time curves of Fig. 18 show the progress of the reaction austenite to ferrite and pearlite at 1320 degrees Fahr. (715 degrees Cent.) in four 0.55 per cent carbon steels with increasing silicon content. Clearly the higher silicon steels are the more rapid as to transformation rate, even though a small addition of chromium was made to prevent graphitization. The proeutectoid ferrite is so clearly set apart in the microstructure that its proportion
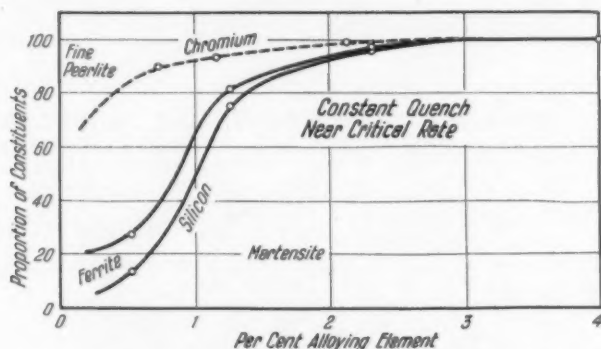
Fig. 19—The Relative Proportion of Martensite and Nodular Fine-pearlite Resulting from Identical Quenching Conditions as a Function of the Silicon Content of 0.55 Per Cent Carbon Steels. The Effect of Chromium is Also Shown. Note Proeutectoid Ferrite Associated With the Silicon Steels.

is recorded on the chart as a branch at the lower part of each curve. The effect of silicon to shift the eutectoid concentration to lower carbon content is well indicated by the decrease of ferrite proportion. It might appear that silicon, along with the other elements which raise the critical points in steel, should contribute to shallow hardening. However, another more decisive experiment disproves this hypothesis. Pieces of the four steels were symmetrically imbedded in a large mass of 18-8 stainless steel, the whole then heated to 1750 degrees Fahr. (955 degrees Cent.) and quenched into brine. The pieces each had, therefore, an identical, accurately controlled cooling rate. The center of each specimen was examined for its content of martensite and fine pearlite. The influence of silicon to induce deep hardening is reflected in the high proportion of martensite in the high silicon steels as shown in the chart of Fig. 19, which indicates also the greater deep hardening effect of chromium. An element contributing to high reaction rate near $A1_e$ may therefore at the same time retard the critical quenching rate for the steel.

Aluminum—Until recently aluminum was so rarely employed as an alloying element in steel that no general familiarity has been

acquired as to its primary effect upon hardening. In amounts up to about 0.15 per cent it exerts marked secondary effects in the steel but little, if any, elemental aluminum remains. Under a subsequent heading evidence will be adduced that the fundamental alloying effect of aluminum is toward deep hardening. The deoxidizing elements silicon, aluminum and vanadium will be treated further under the discussion of oxygen.

Among elements contributing to deep hardening we may include nickel, manganese, chromium, silicon, and aluminum. When present at least to the extent of a few per cent, cobalt, tungsten, vanadium, and probably molybdenum are accelerators of reaction rate and contribute to shallow hardening. Tungsten, cobalt, vanadium, and probably molybdenum all cause such restricted grain growth that it is impossible to say with any assurance just what their primary effect upon hardening might be if the steels with increasing amounts of these elements were studied at a grain size adjusted constant for all.

The contribution of an element alloyed with the steel may not be predicted by its effect upon the critical points nor by its effect upon the reaction rate at a temperature far removed from that which produces the maximum rate of reaction.

Dissolved Oxygen and Normality

To some extent it has been possible to examine into the hardenability of similarly made steels, differing chiefly with respect to the concentration of one element, and to evaluate therefrom the primary contribution toward hardenability (positive or negative) of that element. In many cases at least, we have been reasonably sure that the effect observed was caused simply by the element actually dissolved in the austenite about to be quenched. In other cases the effects seemed rather to depend upon some less direct influence of the added element, a secondary effect, which made its appearance with the first small additions. Now the most reasonable explanation of these vagaries, which interfere with the simple composition effect, would seem to be that there is interaction of some sort between the added element under consideration and some other supernumerary element. It is our persuasion that this disturbing element is oxygen and that its influence is very profound, in spite of its relatively low solubility in the austenite. Before considering these interactions the primary effects of oxygen itself should be investigated, i.e., when

it is dissolved in austenite in the same manner as nickel, chromium, or silicon. Under a subsequent heading, which we now believe is much more important than the present one, oxygen, not in solution, will be discussed, but our immediate interest, we venture to reiterate, is in that oxygen which either is in true solid solution or may be dissolved in the austenite about to be quenched, however small the amount may be. The main difference, it has seemed to us, between oxygen and the other elements, which are alloyed with steel, is that the dissolved oxygen content is so largely dependent upon the concentration of other elements. For example, high contents of both dissolved oxygen and dissolved aluminum or silicon are certainly incompatible in solid steel at heat treating temperatures, and probably even near the melting point in the case of aluminum. One cannot successively add a few thousandths of a per cent of "ferro-oxygen" to the melts, regardless of their composition otherwise, and then secure a series of steels of increasing dissolved oxygen content, as one might well do, for example, with platinum. And yet, in effect, that is precisely what one must do in order to study the effect of dissolved oxygen. We may perhaps employ rather pure irons in which we have introduced sufficiently different amounts of dissolved oxygen for definite contrast.

Now, having ventured thus far into a discussion of "oxygen", it must be said that we are thinking of the word as having quotation marks permanently attached. It is our persuasion, however, that we are really discussing the dissolved element oxygen, although our experiments may include the possibility of this "oxygen" being itself a complex (hydrogen, nitrogen, etc.). (In using the word "complex" we do not do so precisely in the sense of one of our friends who attributes the "oxygen complex" to us personally, not to the steel.)

It will be recalled that McQuaid and Ehn utilized the microscopic appearance of the slowly cooled pack-carburized specimen as a measure of the probable hardenability of carburizing steels. To the specimens with the microstructure which they found to be universally correlated with high hardening capacity in the carburized steel, they applied the word "normal", and to the others the word "abnormal". To be sure, they were interested in eliminating soft spots from a thin hardened case, but the element of fundamental hardening capacity is the same as in high carbon steels. That these words "normal" and "abnormal" have not turned out to be very happily

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applied has been the concern of many metallurgists, among them McQuaid himself, who recently remarked that he sometimes wondered if the terms had not been better reversed, in view of the extended use of the test. But this matter of names shall not be our concern today, for rather, we are more interested in McQuaid's and Ehn's inference that dissolved oxygen was responsible for the low capacity for hardening and the attendant abnormal structures. Again, in the fifth Campbell Memorial Lecture, Dr. M. A. Grossmann offered an array of data and conclusions therefrom sufficient to convince the most skeptical of the fact that oxygen plays an extremely important role in the normality-abnormality story. For these reasons we have grouped the dissolved element oxygen and the normality-abnormality phenomenon under one heading; it seems impossible to discuss them separately.

The Essence of Normality

The essentials of the McQuaid-Ehn test are about as follows:

1. The steel is pack-carburized, for example at 1700 degrees Fahr. (925 degrees Cent.), so that a distinctly hypereutectoid surface layer is developed. If the steel originally contains more than about 1.15 per cent carbon it need not be carburized, but the structure may not be the same as would be developed with carburizing.

2. The carburized steel is then cooled down to about 1150 degrees Fahr. (620 degrees Cent.) at a suitable, definitely controlled rate, after which it may be cooled as convenient,—even quenched. The rate may vary over considerable range for purposes of comparing one steel with another but the rate once selected must not vary for the several runs of the comparison. We have employed a uniform rate of about 4½ degrees Fahr. (2½ degrees Cent.) per minute for our experiments.

The resulting structures, illustrated in Figs. 20 and 21, vary from one steel to another with extremes somewhat as follows:

Normal—Thin, smooth carbide envelopes entirely contiguous with the finer lamellar pearlite.

Abnormal—Thick carbide envelopes, with coarse pearlite, if any, broadly separated from the network by a wide band of ferrite. Usually the carbide is somewhat spheroidized—even the network may be broken with large carbide lumps. There are, of course, all possible degrees of normality-abnormality represented by intermediate structures between the extremes shown; five types have been con-

Fig. 20—A Typical Normal Microstructure. × 1000.

veniently recognized in the studies reported in this dissertation.

It has been suggested that the ferrite band between the carbide envelope and the coarse pearlite area in the grain center forms after the pearlite has originally filled the grain. This seemed doubtful, in view of the extreme slowness of the similar process of spheroidation of pearlite, and an investigation of the mechanism of the formation of an abnormal structure was made. Samples were quenched during the progress of transformation. In Fig. 22 is shown the originally austenitic grain with its carbide envelope just formed, the remainder of the grain being still wholly austenitic as quenched. From this point the real differentiation begins, although even here the carbide envelope is often thin in the normal or deep hardening steel and thicker in the abnormal shallow hardening steel, indicating the supersaturation of austenite in the case of the sluggish deep
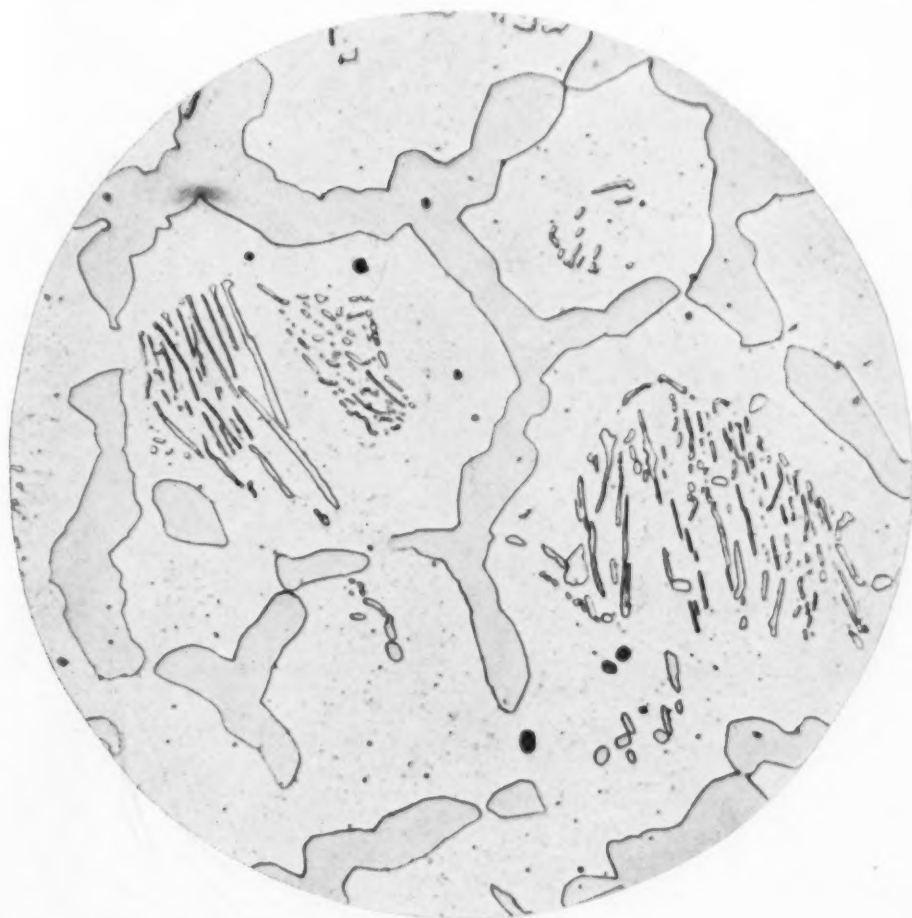
Fig. 21—A Typical Abnormal Microstructure. × 1000.

hardening steel.   But in the photomicrograph of Fig. 23 is shown
the progress of the reaction made in the next few minutes.   A rim
of pure ferrite now separates the carbide envelope from the un-
changed austenite (martensite as photographed) and the eutectoid
carbon has clearly migrated from the austenite through the ever-
widening ferrite band to attach itself to the proeutectoid carbide
envelope.   This process can continue in the thoroughly abnormal
steel until the carbide is wholly interstitial and no lamellar pearlite
is to be found, as in Fig. 24.   In the normal steel, lamellar pearlite
is formed immediately the first particle of ferrite is rejected and
there is no divorce of cementite and pearlite.   An example of this
type of mechanism is shown in Fig. 25.

We offer here an explanation of this variation in terms of rates.
The diffusivity, i.e., rate of diffusion, of carbon in ferrite increases

Fig. 22—The Structure of an Abnormal Carburized Steel Just at the Conclusion of Proeutectoid Cementite Rejection.   × 1000.

tremendously with temperature. The time required at different temperatures for carbide to coalesce into equal sized particles and therefore to contribute equal hardness is a measure of diffusivity. Fig. 26 shows how relatively rapidly the carbon diffuses at higher temperatures. Just below the true $A1_e$ point ferrite forms from austenite more and more slowly with higher temperature. This rate limits the rate of possible broadening of the ferrite rim just inside the carbide envelope.

To produce an abnormal structure, carbide must diffuse more rapidly through ferrite than the ferrite is formed in the rim just inside the carbon network; otherwise simultaneous ferrite and carbide rejection, i.e., pearlite formation, will result. Hence an abnormal structure requires (1) a steel with sufficient transforming

Conclusion
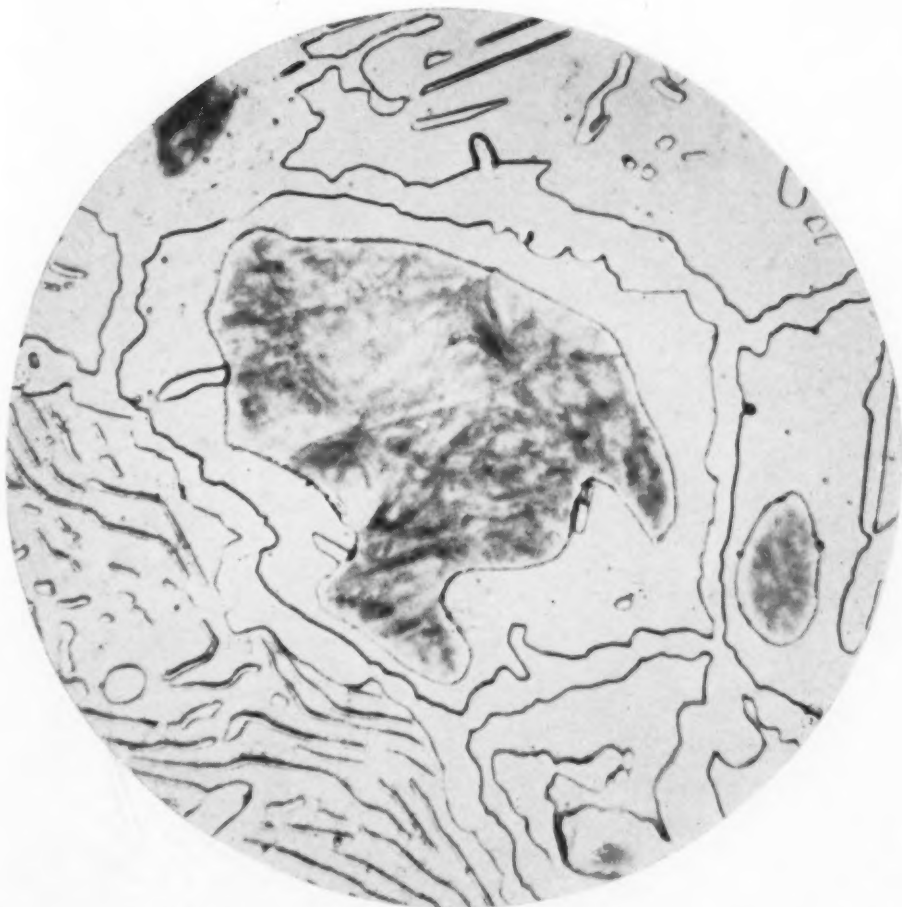
Fig. 23—An Austenite Grain in Abnormal Carburized Steel Forming the Ferrite Rim Inside the Carbide Network Prior to the Formation of Pearlite. × 1000.

rate to prevent under-cooling to temperatures of slow carbide migration, and (2) a carbon diffusivity at this high transformation temperature sufficient to prevent pearlite formation. An abnormal steel then is one of the fast-reacting type but of peculiarly high carbon diffusion rate near but below the true critical point. Now a high carbon solubility in ferrite near $A1_e$ could account in part for high diffusivity, and higher oxygen might in turn induce a higher carbon solubility. Or, if it should happen that high oxygen raised the $A1_e$ critical point even slightly, it would account for the extra carbon diffusivity during transformation, but unfortunately for our speculation this is not found to be the case. However, with the major requirements for abnormal behavior in mind, let us turn to oxygen itself.
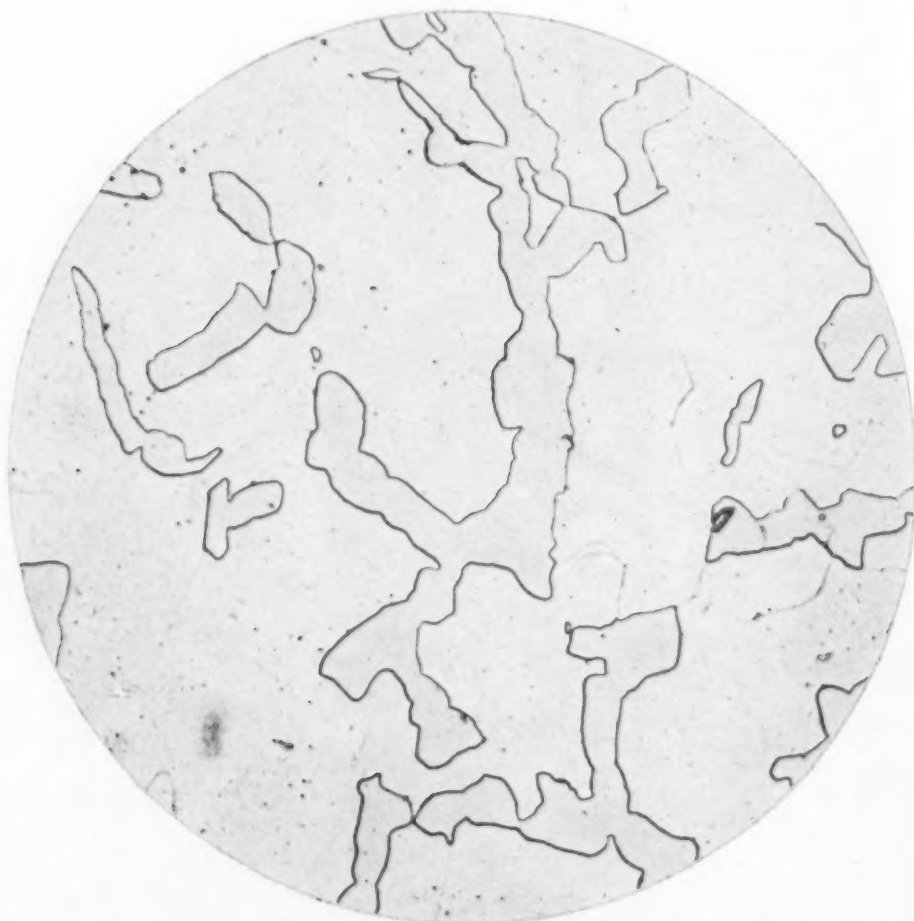
Fig. 24—An Abnormal Carburized Steel Just Transformed Without Any Pearlite Formation. × 1000.

Iron, Carbon and Dissolved Oxygen

Grossmann and others have shown that during pack carburization, with the CO-generating type of carburizers, oxygen is led into the steel along with the carbon. There is ample supplementary proof of this occurrence, even should one doubt the accuracy and dependability of the vacuum carbon-fusion method of determining oxygen. On the other hand, it is inconceivable that pure hydrocarbons and hydrogen could introduce oxygen into a steel. We have therefore used pack carburization as a means of manufacturing high oxygen steel, possibly even saturated with respect to oxygen, and, to secure low oxygen steel we have employed hydrocarbon carburization. We were fortunate to have the assistance of B. M. Larsen and T. E. Brower, who made available a source of oxygen-free hydrocarbon-
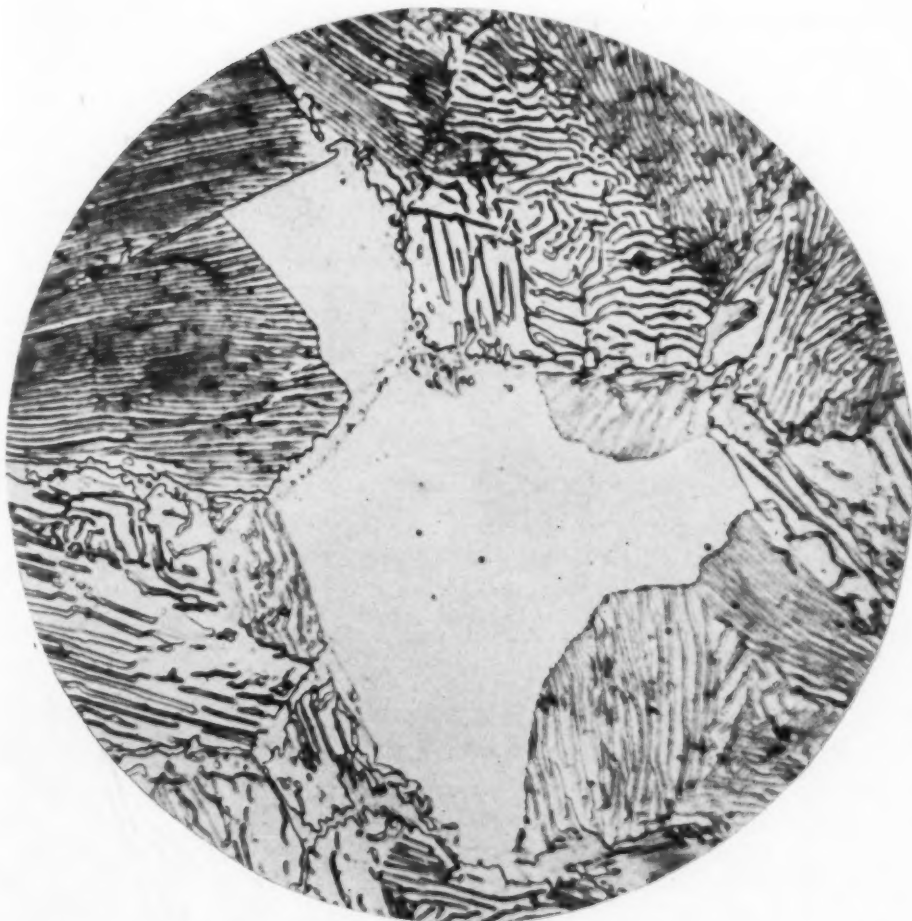
Fig. 25—The Mechanism of the Formation of Pearlite in a Normal Steel with No Ferrite Rim. × 1200.

saturated hydrogen such as is involved in their modified Ledebur oxygen method.[3]   On some fifty steels carburized by the two methods no exception was found to the rule suggested by Grossmann that oxygen-free carburization produces a more normal appearing structure than pack carburizing.   Thus it is not uncommon to find in the same steel the structure of Fig. 27 after pack-carburizing and that of Fig. 28 after oxygen-free carburizing.   According to determinations made by the Larsen-Brower modification of the Ledebur method the diffusible oxygen is increased by pack carburization and reduced by oxygen-free carburization.

We have therefore corroborated the belief that oxygen is the

[3] B. M. Larsen and T. E. Brower, "Critical Studies of a Modified Ledebur Method for Determination of Oxygen in Steel," *Transactions,* American Institute of Mining and Metallurgical Engineers, 1932, Vol. 100, Iron and Steel Division, p. 196-227.

outstanding common element contributing to abnormality in ordinary low carbon steels, provided steels of extremely fine grain are not included, for we have seen that an appearance of abnormality is induced by this factor alone.

There has been some discussion about the normality of "pure" iron-carbon alloys. "Pure" iron is such a vague designation that it
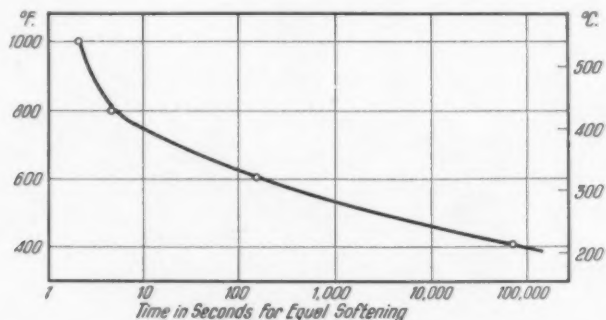
Fig. 26—The Time Required for a Definite Degree of Carbide Coalescence in Martensite at Various Temperatures. Carbon Diffusivity is a Function of Temperature.

seemed best to test out a variety of pure irons from widely different sources, with the assumption that whatever impurities were found in the one were probably not the adulterants of the other. The irons employed were as follows:

1. Electrolytic iron (2 sources).
2. Electrolytic iron remelted in vacuo.
3. Hydrogen-reduced iron, pressed, sintered, and swaged (3 sources).
4. Low oxygen iron from the Westinghouse Electric and Manufacturing Company. (Courtesy Dr. T. D. Yensen) (2 samples).
5. Pure iron from the Westinghouse Electric and Manufacturing Company. (Courtesy Howard Scott) (2 samples).
6. Ingot iron melted and cast in hydrogen.
7. Hydrogen-treated iron from Bell Telephone Laboratories. (Courtesy Dr. P. P. Cioffi).

All developed the abnormal structure in pack-carburizing and the first five showed pronounced abnormality in oxygen-free carburizing, although the ingot iron, melted and cast in hydrogen, was not quite so abnormal as were the others. But the Cioffi iron, carburized in pure hydrogen and hydrocarbon, was almost entirely
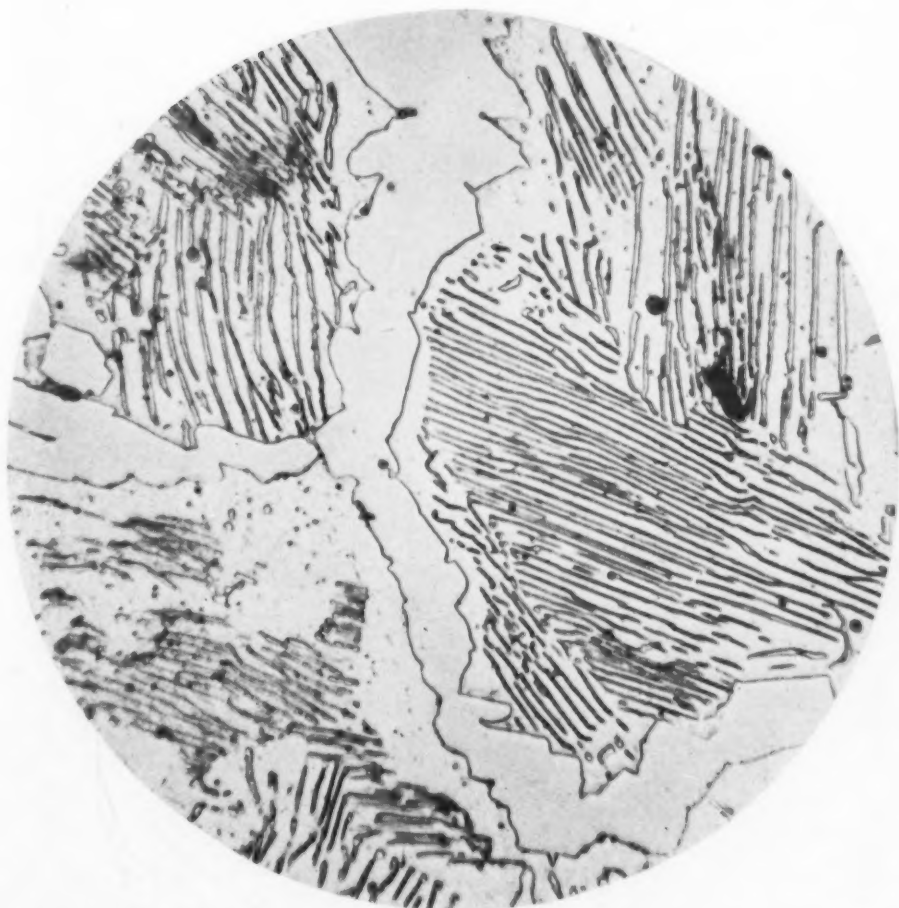
Fig. 27—A Semi-killed 0.06 Per Cent Carbon Steel as Pack-carburized and Slowly-cooled for McQuaid-Ehn Test. × 1000.

normal, as shown in Fig. 29, and possessed an extremely coarse grain size. This iron was produced from ingot iron by heating in pure moist hydrogen for 18 hours at about 2700 degrees Fahr. (1500 degrees Cent.) and had the following analysis:

C	S	Mn	P	Si	O	N
0.005	0.003	0.028	0.004	0.0012	0.003	0.0001

When carefully cooled in pure hydrogen the iron has most amazing magnetic properties,—a maximum permeability of 200,000 and 6,000 as extrapolated to zero magnetizing force. Now whether or not the treatment succeeds in producing a hydrogen alloy or merely a really oxygen-free alloy is open to question. The latter is probably true regardless of the former. In any event the pure iron study permits drawing the following conclusions:
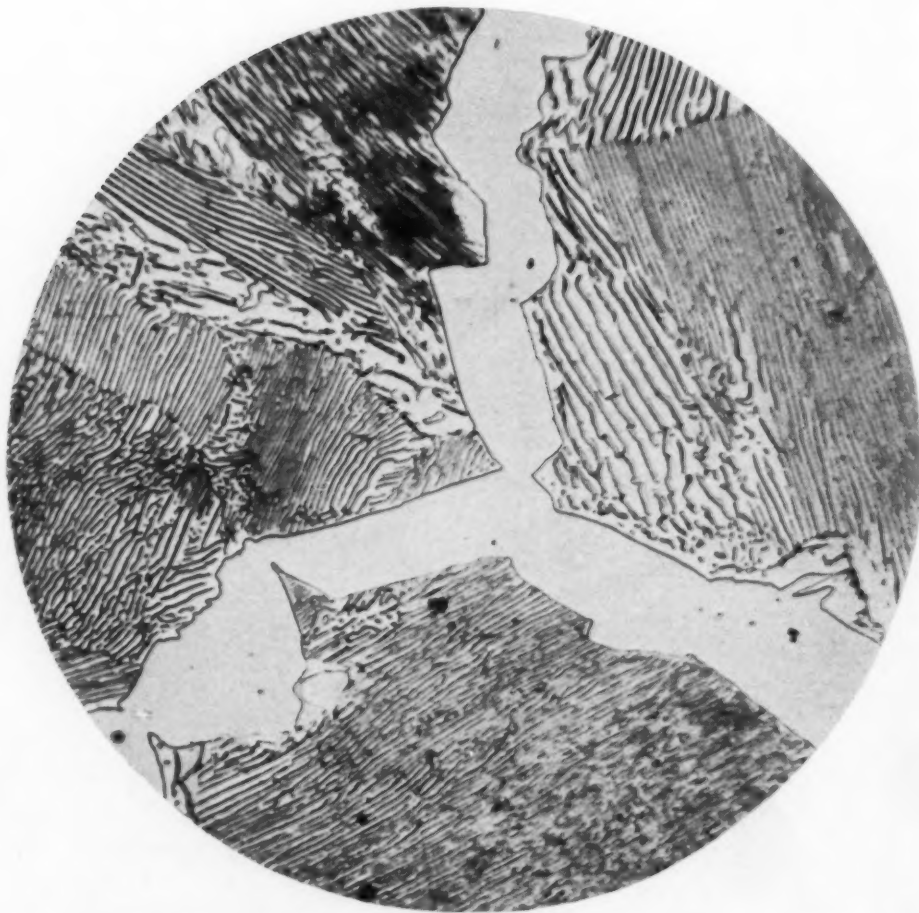
Fig. 28—The Steel of Fig. 27 as Carburized in Hydrocarbon and Hydrogen and Slowly Cooled at Standard Rate for McQuaid-Ehn Test.   × 1000.

1.   To secure a normal structure with pack carburizing requires the presence of some alloying elements of the deep hardening type.

2.   Pure oxygen-free iron, (perhaps with hydrogen in solution) is normal; obviously this implies oxygen-free carburizing.

Houdremont has stated that pure iron is abnormal and suggests that any elements which lower the transformation temperature make for normality; presumably he used the standard test involving pack carburizing and was therefore dealing with high oxygen iron, regardless of his starting material.   His assumption of purity being the cause of abnormality cannot therefore apply so far as oxygen is concerned, and it may be interesting to discover the effect of oxygen upon the true lower critical point.   Only methods depending upon securing equilibrium were relied upon, a time of 16 hours at constant temperature being found sufficient to induce constant con-
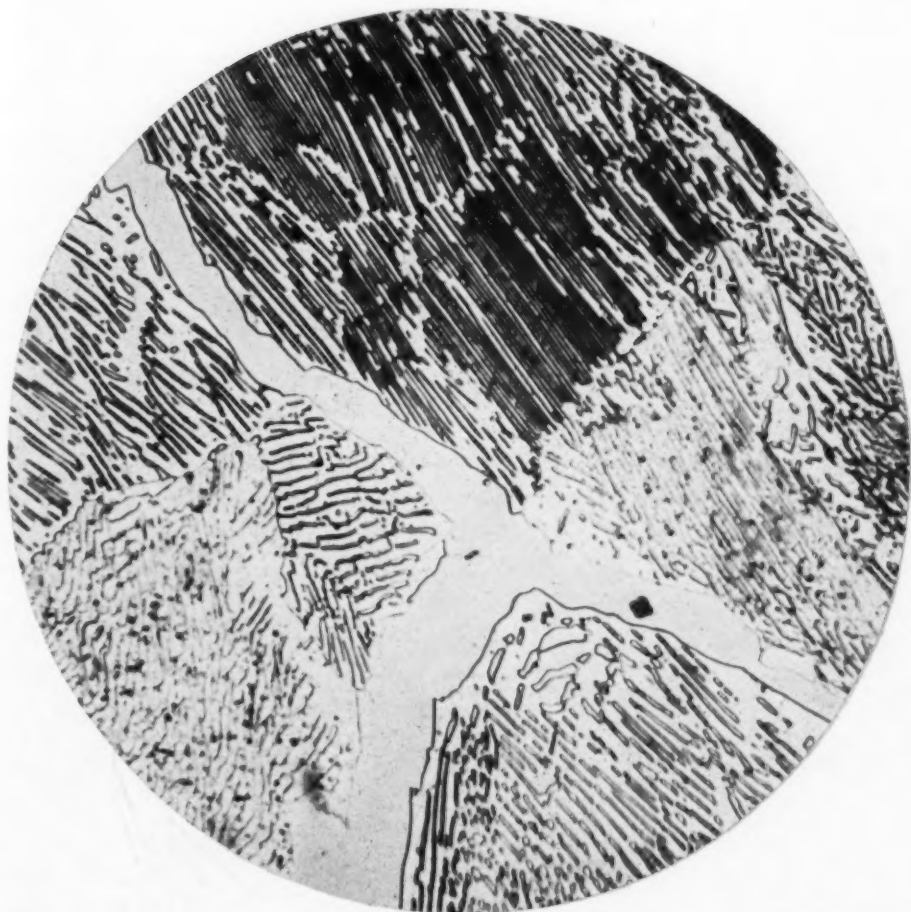
Fig. 29—The Hydrogen-treated Iron of Cioffi as Carburized in Hydrocarbon in Absence of Oxygen. × 1000.

stitution in the region of the $A1_e$ point. For comparable specimens, low and high in oxygen, with the other elements constant, steels were prepared from low carbon irons by the two methods of carburizing. Thin strips were carburized throughout the section to about 1.30 per cent carbon. A very pure electrolytic iron (except for oxygen) was used for one comparison; a 0.40 per cent manganese effervescent 0.06 per cent carbon steel was employed for another comparison to represent a more nearly commercial analysis. In both steels the $A1_e$ range was about 9 degrees Fahr. (5 degrees Cent.) lower in the oxygen-rich material, as shown in Table I. Essentially the same results were obtained from the Cioffi iron as with the electrolytic iron.

Oxygen then is an element which, as dissolved, lowers the true critical point, $A1_e$, and at the same time provides the high reaction

rate and high carbon diffusivity responsible for abnormality. The next step would seem to be the comparison of our synthetic high and low oxygen steels with respect to relative hardenability.

Reasoning from the contribution of dissolved oxygen to the formation of the abnormal structure in nearly pure iron-carbon alloys, we were led to assume that this oxygen would strongly contribute to shallow hardening, but to date we have been unable to prove this point. Experimentation has been carried out by prepar-
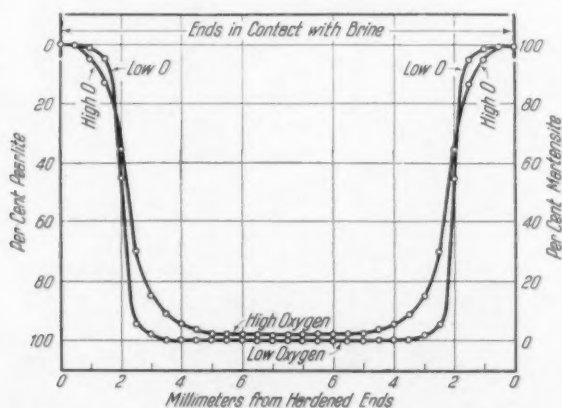
Fig. 30—The Proportion of Martensite and Fine-pearlite in Cylinders of Low and High Oxygen Synthetic Steels as Hardened in Stainless Steel Disks. The Fully Martensitic Ends were in Contact with the Quenching Brine.

ing high carbon steels from slender cylinders of very pure electrolytic iron. Half the cylinders were pack-carburized and half were hydrogen-treated and likewise carburized but in oxygen-free hydrocarbon gas. Various low metalloid steel wires were likewise carburized by the two methods and all were tested for depth of hardening. The greatest difficulty was encountered in securing similar austenitic grain size and the results therefore are not absolutely final, although actually the grain size discrepancy throws much weight on the unsuspected circumstance that dissolved oxygen has only a very slight effect upon depth of hardening and conceivably in the direction of deep hardening. Briefly, the cylinders were inserted in disks of stainless steel and heated to dissolve all the finely divided carbide, then cooled to form a cementite network and finally quenched in brine. Fig. 30 shows the relative proportion of martensite and nodular fine pearlite in the cylindrical specimens determined by microscopic examination from end to end. The chart is the average

Table I

Lowest Temperature in the Al$_e$ Range

	Pack-Carburized High Oxygen	Gas-Carburized Low Oxygen
Electrolytic Iron	723 degrees Cent. (1333 degrees Fahr.)	728 degrees Cent. (1342 degrees Fahr.)
Effervescent Steel	718 degrees Cent. (1324 degrees Fahr.)	724 degrees Cent. (1335 degrees Fahr.)

of a great many closely agreeing determinations and is representative of all the pure iron-carbon alloys examined. Perhaps the most that may be said is that dissolved oxygen does not affect hardening capacity markedly, for the possible experimental errors render precise conclusions unwarranted. The figures presented do indicate, however, that dissolved oxygen favors the formation of some martensite but not the complete prevention of some small amount of transformation to fine pearlite. These synthetic pure iron-carbon alloys harden much less deeply than even the most shallow hardening commercial high carbon steels, and we are led to believe that possibly no steel could show lower hardening capacity than an uncoarsened pure iron-carbon alloy.

We conclude then that the ferrite-rim type of abnormality is the particular contribution of dissolved oxygen, which, on the other hand, does not itself contribute significantly toward shallow hardening. In seeking a more universal feature of the pack carburizing test we are led to the quality of the pearlite as an indicator of hardenability. Fine and regular pearlite lamellae are the general indication of deep hardening steels, while fine grains and coarse irregular pearlite connote shallow hardening.

Abnormality and Inherent Grain-size Tendency

The case for inherent grain size as a major influence upon hardenability grows increasingly strong, and it should be remembered that McQuaid and Ehn found that in most cases abnormality accompanied small grains even in their carburizing steels. We have seen that a fairly coarse abnormal grain is not impossible, indeed this combination was carefully selected for the study of dissolved oxygen. But it is the exception and no very great differences between the abnormal and normal in those synthetic low metalloid steels were found with respect to hardenability. On the other hand, it has been shown that, other things being equal, the fine-grained austenite

Fig. 31—Normal Structure in a Carburized Pure Iron-Aluminum Alloy Containing
0.50 Per Cent Aluminum. × 1200.

transformed more rapidly, appeared more abnormal as cooled, and hardened less deeply than the coarse. Now in the case of heat treating steels a finer grain size may be induced than any examined in our comparisons, provided the steel is manufactured in a manner to restrict grain growth effectively. It is possible now to inquire whether austenite grain size may not be a vastly more important factor in determining hardenability than dissolved oxygen. It is our thought that this is true, but that oxygen is still a factor.

Reasoning from the method of controlling grain size in pure tungsten filament wire by the incorporation of a fine dispersion of inert thoria particles; it has seemed to us that the ideal way to maintain a fine austenite grain would be to disperse in the steel a system of fine oxide particles. Accordingly, we have been inclined to accept the hypothesis of those who have suggested dispersed alumina as

Fig. 32—Shower of Particles Formed in the Outer Hypereutectoid Zone of a 0.50 Per Cent Aluminum Pure Iron-Aluminum Alloy by Means of Pack Carburizing. Such Particles are Absent in the Oxygen-free Carburized Material. $\times$ 3500.

one cause of fine grain and abnormality. Several years ago Epstein[4] observed that late additions of aluminum (as in the ingot mold) seemed to result in abnormality. Other highly stable, and therefore insoluble oxides would serve as well, and vanadium appears to function in this way. If the particles which are to act as a grain growth inhibitor, by what Jeffries terms "mechanical obstruction" are to be formed *in situ* in the molten steel then the steel must contain sufficient oxygen to combine with the needed amount of alloy and no substantial coalescence must occur; neither requirement is incompatible with effective practice. The direct experimental enquiry into the existence and nature of minute particles, which, to be most ef-

[4]S. Epstein and H. S. Rawdon, "Progress in Study of Normal and Abnormal Steel," TRANSACTIONS, American Society for Steel Treating, Sept. 1927, Vol. XII, p. 337-375.

Fig. 33—Photomicrograph of 1.0 Per Cent Carbon Steel Carburized for McQuaid-Ehn Test Illustrating the General Trend of Coarse Grains Toward Normal Structure and Fine Grains Toward Abnormality. $\times$ 1000.

fective, must remain practically submicroscopic, seems at the moment impossible, but a few more or less indirect observations may be considered.

Aluminum Contributes to Normality—Aluminum was not discussed with the other alloying elements on account of lack of data on its primary effect in hardenable steels.   However, a series of pure iron-aluminum alloys was prepared in a manner to retain as much of the elemental aluminum as possible in true solid solution in the finished alloy.   When such alloys carrying more than about 0.4 per cent aluminum were carburized in hydrocarbons the structure was highly normal throughout, as shown in Fig. 31.   In contrast, when pack-carburized, they developed a very fine-grained, abnormal structure in the outer portion of the hypereutectoid zone.   This outer

zone was further characterized by a shower of fine particles, shown in Fig. 32, which we assume to be alumina,—entirely absent in the specimens carburized in hydrocarbons. Inside this zone the two methods of carburizing produced identical normal structures. We interpret these observations as indicating the alumina particle inhibition to grain growth by the combination of aluminum (contributing itself toward normality) with oxygen introduced in carburization.
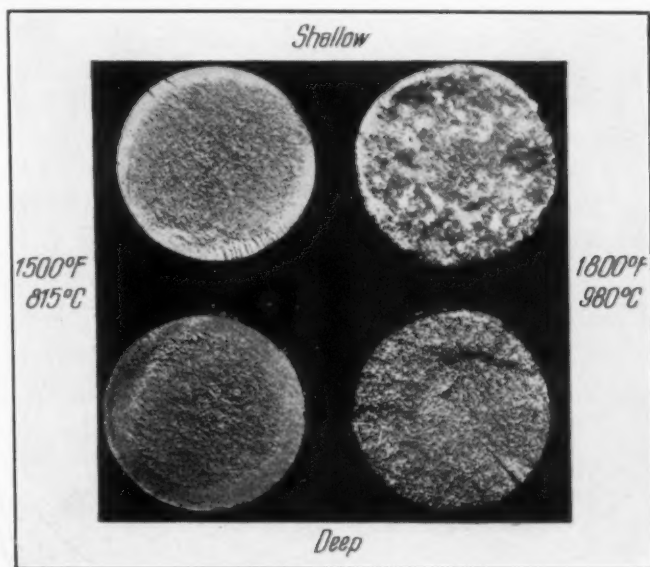
Fig. 34—Fractures of Two 1.0 Per Cent Carbon Steels as Normally Quenched, and as Coarsened at 1800 Degrees Fahr. (980 Degrees Cent.) Prior to Quenching. Note Exaggerated Grain Growth in Fine-grained Steel Due to Long High Temperature Heating.

The aluminum combined so vigorously with the oxygen that only a shallow layer was affected; the higher the aluminum content the thinner the surface zone of abnormality. We are therefore persuaded that the usual small additions of aluminum contribute to shallow hardening, but solely by grain growth inhibition offered by the dispersed insoluble alumina particles.

While we have spoken of effective grain size as though merely the dimensions of the average grain were involved, it should be stressed that undoubtedly it is the peculiar energy condition in the grain boundary material which is responsible for the vast difference between austenite of fine and of coarse grain. The total amount of the interface material, i.e., in the compromise zone between grains, varies rapidly with grain size. This variation is the significant one.

To secure a normal test structure by the standard McQuaid-Ehn procedure demands the presence, along with carbon and iron, of an element contributing to deep hardening, or at least one reducing oxygen solubility materially, such as silicon or aluminum. In general, steels appear more and more abnormal as the grain size diminishes, a fine-grained normal steel requiring both the presence of deep hardening elements and a grain growth inhibitor. A coarse-grained abnormal structure connotes a steel low in the elements contributing to deep hardening and in the elements reducing oxygen solubility.

Elements Contributing Shallow Hardenability Also Restrict Grain Growth

It will be recalled that tungsten and cobalt were listed as elements which positively diminish depth of hardening but it was reserved for this chapter to stress the fact that both elements greatly reduce the grain growth tendency in the austenite. Houdremont's evidence is conclusive for cobalt and our own experience with a tungsten series resulted in a complete failure to secure a grain size in the four per cent alloy comparably coarse with that in the one-half per cent tungsten steel. Now it seems highly improbable that either cobalt or tungsten may form fine oxide particles to offer "mechanical obstruction," but they may, merely by solid solution alone, raise the temperature for grain growth above that employed in our experiments, say 1900 degrees Fahr. (1040 degrees Cent.). Possibly, fine, slowly dissolvable carbide particles might inhibit grain growth in tungsten steels but not in the cobalt steels. One cannot but correlate other properties of high tungsten steels and wonder, if equal grain size were securable, whether these two elements might not make for deep hardening.

Hardenability of Plain High Carbon Steels

Fine tool steels of low alloy content show a marked variation in capacity to harden, even though their ordinary chemical analysis suggests no explanation for this behavior. In 1929 G. V. Luerssen[5] described this matter in detail. The McQuaid-Ehn test, even in these high carbon steels, serves to predict hardenability, but the grain size is the principal criterion and the abnormality is not of the marked

[5]G. V. Luerssen, "Some Notes on the Behavior of Carbon Tool Steel on Quenching," TRANSACTIONS, American Society for Steel Treating, Feb. 1930, Vol. XVII, p. 161-192.
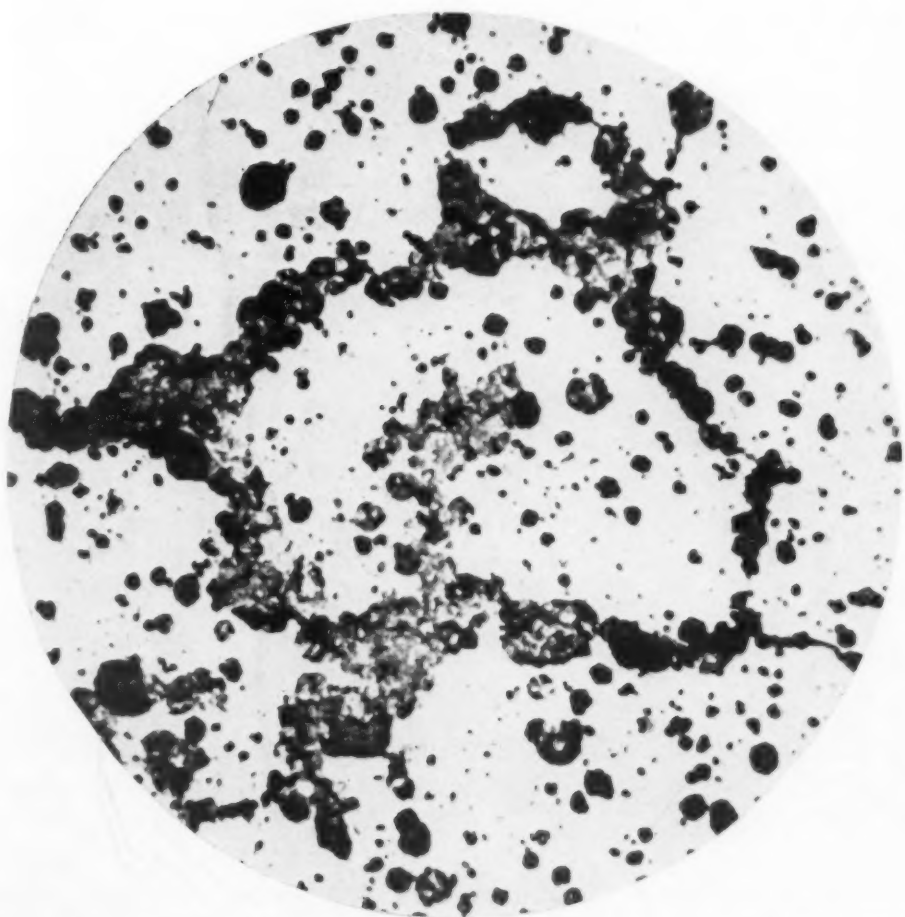
Fig. 35—Photomicrograph of Shallow Hardening 1.0 Per Cent Carbon Steel With Coarsened Grain. × 1000. Note Transformation Nuclei Dispersed Through Austenite Grains.

ferrite band type. In the steel of intermediate hardenability one frequently finds the mixed grain size, coarse—normal, fine—abnormal, as illustrated in the photomicrograph of Fig. 33. This circumstance would now appear inevitable if any marked inhomogeneity in the austenite existed. We have had all too little to say of these standard steels upon which our interest should center,—mainly because coarse-grained normal and abnormal structures in nearly pure irons were required for the dissolved oxygen study, and for grain size effects alone impracticable heat treatments were necessary, and because the primary effects of alloying elements could only be estimated in high alloy steels. However, we may conclude the assembling of evidence by a reference to one or two observations on high carbon steels.
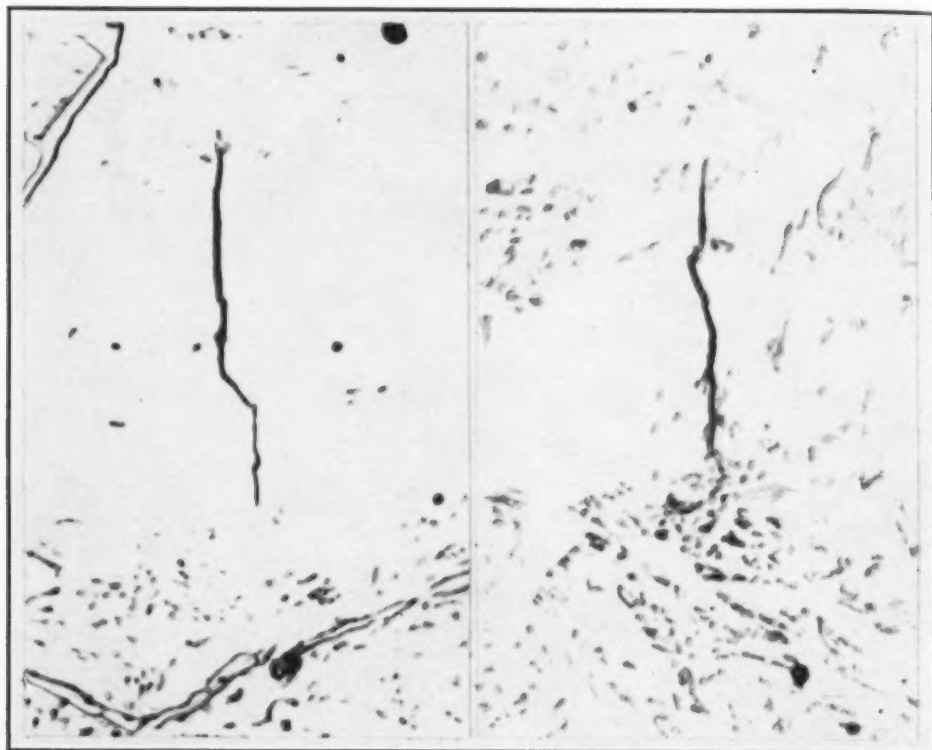
Fig. 36—Typical Martensite Cracks, as Described by Lucas, in Coarsened Steels Quenched (left) From Only 1375 Degrees Fahr. (745 Degrees Cent.) (right) From 1725 Degrees Fahr. (940 Degrees Cent.) × 2500.

A coarse-grained deep hardening 1.0 per cent carbon steel coarsened markedly at 1500 degrees Fahr. (815 degrees Cent.), while a shallow hardening steel of almost identical analysis remained very fine. When both were heated for several hours at 1800 degrees Fahr. (980 degrees Cent.), however, the fine-grained steel acquired a relatively enormous grain size nearly ⅛ inch in average diameter, while the coarse steel remained about as at 1500 degrees Fahr. (815 degrees Cent.). The fractured sections of Fig. 34 show the exaggerated grain growth. This behavior is strongly suggestive of the elevation and intensification of the germinative range brought about by mechanical obstruction, i.e., dispersed particles.

Another very shallow hardening steel of tremendous induced grain size was, however, still shallow hardening and the photomicrograph of Fig. 35 may perhaps show the reason. This specimen was coarsened and then quenched at a rate just short of the critical quenching speed and contains therefore some fine pearlite. It will be seen that the particles which inhibit grain growth are also nuclei

or transformation centers, much as though they still determined the grain boundaries. So far as deep hardening is concerned, the steel might almost as well still have its fine grain. Not all inhibitors remain effective in this manner, and some clearly dissolve and coalesce at coarsening temperatures.

The well-known superior toughness of the fine-grained type of steels has interested us. In breaking many specimens later observed in the microscope a correlation was unescapable that brittleness was associated with the minute cracks described by Lucas[6] and shown in Fig. 36. When they became very prevalent the specimen was invariably visibly cracked in heat treatment. But what is more important, they were not found in the very fine-grained steels, regardless of heating temperature. One of the particular examples photographed was one of thousands in the coarsened steel quenched from only 1375 degrees Fahr. (745 degrees Cent.) previously discussed; the other was found associated with fine pearlite in a coarsened steel referred to previously, Fig. 9. We conclude then that it is not impossible that the cracks discussed by Lucas are the forerunners of the gross cracking of quenched steels and that they are not a result alone of the depth of hardening, nor dependent solely upon the severity of quench, but essentially a matter of actual grain size, influenced, of course, by the mass and contours of the specimen, acting as stress determinants.

CONCLUSIONS

The lines of reasoning, which have been outlined, led us to the following views on hardenability, and related properties of steel.

In the first place hardenability of a steel depends upon the actual rate at which its austenite transforms to fine pearlite at the particular temperature at which this reaction sets in most promptly. The precise temperature at which this rate is greatest depends, of course, upon the composition of the steel; in any case, it is, we believe, this maximum rate at temperatures near 950 degrees Fahr. (500 degrees Cent.), which determines the critical quenching speed which must be exceeded if the steel is to be hardened.

[6]F. F. Lucas, Henry Marion Howe Memorial Lecture, 1931, "On the Art of Metallography," *Transactions,* American Institute of Mining and Metallurgical Engineers, 1931, Iron and Steel Division, p. 11-44.

In the second place, this maximum rate of austenite transformation is in turn largely determined by the condition of the austenite at the moment of quenching with respect to two factors:

(1)   Its composition with respect to dissolved elements, most of which retard, though some may hasten, its transformation to pearlite.   Manganese, chromium, nickel, silicon and aluminum definitely slow up the reaction and so contribute directly to deep hardening about in the order named; on the other hand, tungsten, cobalt, molybdenum, vanadium, and possibly oxygen appear to induce shallow hardening, though most probably indirectly by restricting grain growth.

(2)   Its effective grain size.   The finer the grain size, the more rapid is the transformation to fine pearlite, and correspondingly the lower is the hardenability.   Indeed, effective grain size seems to be the most potent single factor influencing hardenability; it in turn is probably controlled largely, for any specified temperature, by the obstruction to grain growth offered by large numbers of very finely dispersed particles, of exceedingly small aggregate mass, comprised presumably of stable oxides such as alumina, vanadia, and probably silica or silicates.

No one who sets out to ascertain the significant factors in a case as complex as this proves to be, can claim to say the last word on it; on the contrary he is likely to raise more questions than he answers.   Many such questions will doubtless occur to you; two only are put forth as a challenge to a more rigorous examination of the evidence bearing upon these questions:

1.   May it be that the primary influence of any element (including oxygen) in true solid solution in austenite of a specified grain size is to retard the rate of transformation and hence to favor deep hardening?

2.   May it be that the main effective contributor to shallow hardening, apart from the absence of alloying elements, is oxygen combined with elements such as aluminum and vanadium in the form of a fine dispersion of insoluble particles?

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CORROSION RESISTANCE OF IRON-CHROMIUM ALLOYS IN VARIOUS MEDIA

I.   The Salt Spray Test

By W. B. Arness and J. N. Ostrofsky

Abstract

The paper is based on an investigation of the resistance to the salt spray test of the low carbon iron-chromium alloys analyzing about 0.10 per cent carbon and from 12.5 to 26.5 per cent chromium. An aqueous solution of 4 per cent sea salt is used. Test specimens were selected from commercial bar stock. Space is devoted to a discussion of the results in terms of variables inherent in the metal and in the test itself. The effect of various heat treatments is studied. In order to establish the normal quality of the test materials, tensile strength figures and nitric acid corrosion test results for the same materials are reported. A brief discussion of the mechanism of rusting under conditions of the salt spray test is included. Difficulties in exactly interpreting test results are pointed out, and the merits and limitations of the test are discussed. Attention is called to the generally excellent rust resistance of the entire range of alloys studied.

Introduction

THE present paper is the first of a proposed series relating to the behavior of rustless iron-chromium alloys when exposed to the action of various corrosive media, and is concerned specifically with the resistance of certain of these alloys in the salt spray test.   The purpose of the paper is three-fold.   (1) It was desired to call attention to the excellent rust-resisting properties of the iron-chromium alloys which, because of the urgent need for protracted research in the field of the chromium-nickel alloys, have been neglected by many investigators.   (2) to call attention to some of the peculiarities and to the noninfallibility of the salt spray test, and to the resultant complications, when using this testing method as an index to the behavior

of the alloys in service, and (3) to instigate a more critical scrutiny of the salt spray test in the hope that better standard methods for making the test might be worked out.

It is generally known that chromium is highly resistant to corrosion. It is also well recognized that chromium, when added to iron as a substantial alloying constituent, lends to the iron its own corrosion-resistant properties. Many fabricators and users of iron are quite well aware of these remarkable characteristics of iron-chromium alloys, and even the man on the street has some vague appreciation of the rust-resisting qualities of chromium.

It is also well recognized that iron-chromium alloys are not sufficiently noble to resist all corrosive media, nor to be flatly accorded the designation, "non-corrodible," without certain qualifications. Study of the corrosion-resistant properties of the iron-chromium alloys has been found to be exceedingly complex—as complex as the subject of corrosion itself. This complexity has led to many inaccurate predictions of the corrosion-resisting ability of various iron-chromium alloys, and to numerous instances of their misapplication in industry. It has also led to the development of many new alloys built around the iron-chromium combination in various proportions and containing other supplementary alloys, commonly nickel. Some of these alloys have been mistakenly offered over a wider field of application than was proper, and others have been developed for special fields, in many cases with marked success. All are partially or completely resistant to many severely corrosive media and all are valuable contributions to ferrous metallurgy.

As experience with the iron-chromium alloys widened, and some of their limitations and peculiarities were exposed, it became necessary to predict the probable corrosion resistance of these alloys in service by means of laboratory testing methods. Corrosion testing is involved, and there are many pitfalls into which the unwary or ill-advised investigator may fall, particularly in drawing conclusions as to the significance of the results obtained. Resistance of one alloy to one corrosive medium does not necessarily indicate the resistance of other similar alloys to the same medium, or of the same alloy to other media. Many other influences entirely aside from the analysis of the alloy profoundly affect its performance characteristics. Heat treatment, method of assembly, preparation of exposed surfaces, contact with nonferrous metals, conditions of strain or fatigue in service, are important factors which must be considered.

As for service conditions, aside from the corrosive agent itself, such factors as temperature, pressure, purity, galvanic action, presence or absence of oxygen, variation in concentration, nature of flow in containers or lines, must all be taken into account. In addition to these it is necessary to examine the degree and manner of progress of corrosive attack. A given corrosion loss when uniformly distributed might permit commercial use, whereas the same degree of corrosion concentrated in one or many local areas would make the application impracticable.

Out of a great deal of laboratory and service experience a few methods of testing have emerged which, regardless of their sometimes confusing and erratic results, have come into fairly wide use. One of these is the copper sulphate test used mainly for iron-chromium-nickel alloys of the 18-8 type, but also occasionally for some of the iron-chromium alloys. Another is the Huey[1] test which uses boiling 65 per cent nitric acid in a reflux condenser. This test can be used to measure directly the resistance of an alloy to nitric acid, and insofar as nitric acid resistance is a measure or indicator of general corrosion resistance, it is also a very helpful guide. At any rate, it does give reproducible results; and when quality or heat treatment is seriously off-grade, some reflection of the condition is usually seen in this test.

One of the most commonly used methods for determining resistance to the atmosphere, moisture, and water or salt water is the salt spray test. It is not an infallible test, nor has it been entirely standardized, but it is relatively simple and inexpensive to make, and if the material tested has any inclination to rust, the salt spray will reveal it.

One of the earliest references to a salt spray test is that of Capp[2] who used a spray chamber to determine the corrosion resistance of galvanized sheet. Since then the test has been used and developed by many workers.[3, 4, 5] Strauss and Talley[6] reported results on a

[1]W. R. Huey, "Corrosion Test for Research and Inspection of Alloys," Transactions, American Society for Steel Treating, Vol. XVIII, 1930, p. 1126.

[2]J. A. Capp, "A Rational Test for Metallic Protective Coatings," Proceedings, American Society for Testing Materials, Vol. XIV, 1914, Part II, p. 474.

[3]A. N. Finn, "Method of Making the Salt-Spray Corrosion Test." Proceedings, American Society for Testing Materials, Vol. XVIII, 1918, Part I, p. 237.

[4]H. S. Rawdon, A. I. Krynitsky and W. H. Finkeldey, "Types of Apparatus Used in Testing the Corrodibility of Metals," Proceedings, American Society for Testing Materials, Vol. XXIV, 1924, Part II, p. 717.

[5, 6]See bottom of page 432.

large number of iron-chromium alloys after a month's exposure to the spray during the daytime and to the damp chamber at night. The U. S. Navy Department contributed much to the standardization of the salt spray test by issuing careful descriptions of the equipment and technique used, and by basing acceptance or rejection of material upon performance in this test. The salt spray test has also been adopted by other governmental departments and bureaus. Producers and many users of rustless iron employ the salt spray as a collateral but not necessarily final test in their studies of the factors affecting resistance of their products to corrosion.

A word relating to the interpretation of the salt spray test may not be amiss. The degree of attack does not lend itself readily to quantitative measurement, and in fact one of the weakest points of the test is the difficulty of interpreting the results in terms of probable service performance. Specimens are usually judged according to their appearance upon completion of the test. Slight surface rusting or staining is not generally accounted as failure to resist the conditions of test. But the presence of progressive corrosion as evidenced by severe rusting and localized pitting is often considered serious, because material of this character might show evidence of rusting or corrosion under the generally milder conditions of service in salt water, salt air, or average dampness. Occasionally the loss or gain in weight during the test is measured, but this figure will have no significance unless the rusting is uniform (i.e., free from localized pitting).

During the course of routine and investigational work on the low carbon rustless irons, mostly in behalf of the Rustless Iron Corporation of America, the authors have had frequent occasion to observe the workings and results of the salt spray test. In general, the resistance of the tested alloys, particularly in strip form, has been excellent, but some observations have been indeterminate, and especially it has been found difficult to avoid erratic results and to correlate salt spray resistance with resistance to other media. This present paper is based on a brief study of the resistance to the salt spray test of various low carbon iron-chromium alloys ranging in chromium content from about 13 to 26 per cent, all of the material

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[5]H. S. Rawdon, M. A. Grossmann and A. N. Finn, *Chemical and Metallurgical Engineering,* Vol. 20, 1919, p. 462.

[6]J. Strauss and J. W. Talley, "Stainless Steels: Their Heat-Treatment and Resistance to Sea-Water Corrosion," *Proceedings,* American Society for Testing Materials, Vol. XXIV, 1924, Part II, p. 217.

tested being in the form of bar stock. No attempt was made to extend the scope of this paper to include a study of these alloys in strip, sheet, or wire form. The bar stock was selected at random from commercial 9-ton heats and had the sizes and compositions shown in Table I.

Table I

Sizes and Composition of Steels Investigated

Alloy	Size	C	Mn	P	S	Si	Cr	Ni
A	1″ sq.	0.11	0.27	0.024	0.016	0.33	13.23	0.25
B	1″ sq.	0.09	0.32	0.026	0.018	0.19	12.57	0.25
C	¾″ rd.	0.06	0.32	0.028	0.019	0.23	17.38	0.22
D	¾″ sq.	0.10	0.31	0.032	0.021	0.30	17.64	0.21
E	1¼″ sq.	0.15	0.29	0.029	0.015	0.33	17.21	0.26
F	1″ sq.	0.08	0.37	0.030	0.015	0.51	21.80	0.19
G	1″ sq.	0.13	0.33	0.026	0.016	0.48	21.49	0.26
H	1″ sq.	0.21	0.41	0.028	0.021	1.05	26.45	0.20

All of the specimens were heat treated. Previous observations of the iron-chromium alloys in the salt spray test had demonstrated the necessity for heat treatment of the 13 per cent chromium alloys. Above 16 per cent chromium the effect of the heat treatment is not so marked, but it is plainly evident that up to and even above 20 per cent chromium, the hot-rolled material is somewhat deficient in resistance to the salt spray test, and that over heating, resulting in a coarsened grain and concentration of carbides along crystal boundaries, also reduces the resistance of the alloy. But there is not the clear and consistent relationship between resistance to attack in the salt spray, and heat treatment, as there is for instance in the Huey test (65 per cent boiling nitric acid). Since it has also been observed that the iron-chromium alloys above 16 per cent chromium are extremely sluggish in reacting to heat treatment, it was considered advisable to study the effect of long time treatments such that structural changes could proceed to equilibrium, and observe whether these treatments might be a factor in salt spray resistance. For these reasons the treatments outlined in the Table II were selected, and it will be noted that the "time at temperature" periods ranged from 10 hours on the 17 and 21 per cent chromium alloys to 15 hours on the 26 per cent chromium alloy. These treatments will be discussed more fully below.

Cylindrical slugs about 1½ inches long were machined from the bars after removing at least ⅛ inch of surface. A 60-degree cone was then machined on one end of each specimen. The finish-
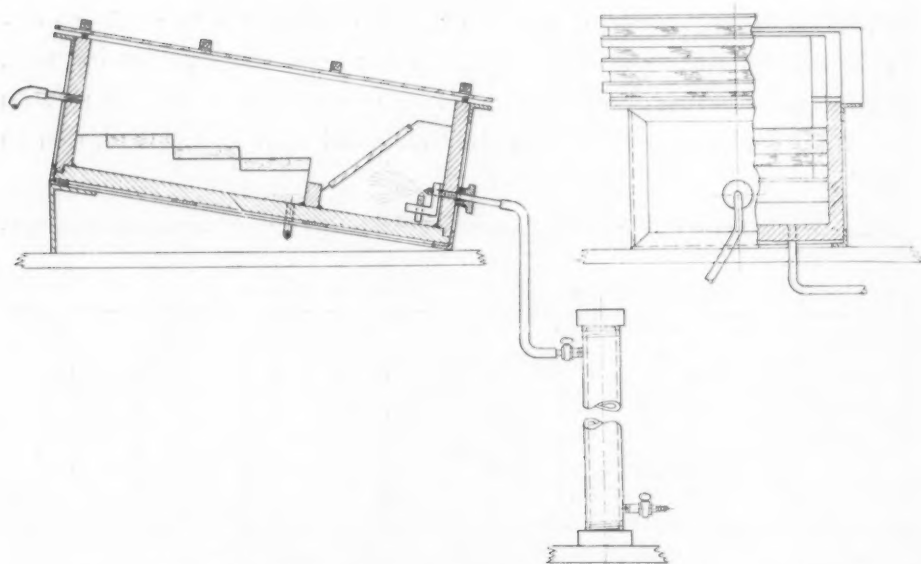
Fig. 1—Form of Salt Spray Chamber Used. Shell is of Alberene Stone. Shelves and Baffle are of Glass. Spray Tips are of Glass Instead of Metal as Shown.

ing cut was very light, and a high speed was used. The tool was ground before taking each finishing cut, and was set to cut as freely as possible. Tool marks were removed with a clean mill smooth file. The final finish was obtained with 00 emery cloth used dry. The emery contained approximately 35 per cent Fe_3O_4. The surface finish was quite rough and lacked entirely the lustre of a polished surface. Triplicate samples were prepared from each bar, and before exposure were carefully cleaned with alcohol and ether. No passivating treatment was given.

Polishing of the surface was deliberately omitted, because it was desired to study the inherent salt spray resistance of the metal, rather than the superficial resistance of a highly polished surface. In this way it was thought that the specimens could be induced to rust more easily, and perhaps would more consistently reflect differences in quality, heat treatment and analysis. Besides, the beneficial effect of polishing is well known, and wherever employed increases the margin of safety against rusting. It was further recognized that rust resistance of an alloy can for many purposes be judged by the probable rate at which the material is destroyed, and for such applications the presence of superficial staining is not objectionable.

Because of its wide use the equipment and technique of the Navy salt spray test are well understood, and these have been utilized in all essential details in making the tests which form the basis

of this paper. The spray chamber was of alberene construction with glass shelves and a glass atomizer, and resembles those described and used by Capp, Strauss, Rawdon, Krynitsky, and the U. S. Navy Department. The chamber was constructed so that no spray drainage returned to the solution reservoir. Fig. 1. The air pressure was 10 pounds per square inch and the air was cleaned by passing through a 10-inch column of water before entering the spray chamber. No attempt was made to conform to any standard dimension of the atomizer tips. It has been observed that slight disturbance of the adjustment of the tips has far more effect on the amount of spray than small variations in size. The spray obtained was quite fine and the chamber was at all times filled with a dense, thoroughly atomized mist. The spraying solution was 4 per cent sea salt in distilled water.

Two sets of specimens were exposed for 500 continuous hours and were undisturbed except for periodical inspection. The third set was also exposed for 500 hours but was cleaned of all corrosion products at the end of each 100-hour period except the last. Tightly adherent rust was softened by immersing for several hours in a solution of 20 per cent ammonium acetate containing 2 per cent acetic acid. This solution has no action on any of the alloys tested.

Justification for the procedure whereby one set of specimens was alternately exposed and cleaned lies in the fact that for almost all atmospheric corrosion conditions, alternate wetting and drying and occasional cleaning would be quite the usual thing. And also for marine service the same conditions would frequently be met. The reasons which suggested that this procedure might yield interesting results were, it must be confessed, somewhat vague and are, therefore, difficult to express. Briefly, however, the inconsistencies often observed in salt spray test results suggested that rusting was closely related to a condition of the surface film involving principles of localized electrochemical attack. Certainly sufficient evidence has been accumulated to indicate that such characteristics as nonmetallic content, chemical segregation, and microstructure are not solely responsible for irregular resistance to rusting in the salt spray. Indeed, the established fact that careful polishing of the surface serves to improve rust resistance is one of the best reasons for attributing this resistance partially to some more or less obscure and superficial surface condition.

It will be clear that two distinct salt spray tests have been investigated, one consisting of 500 continuous hours exposure, which
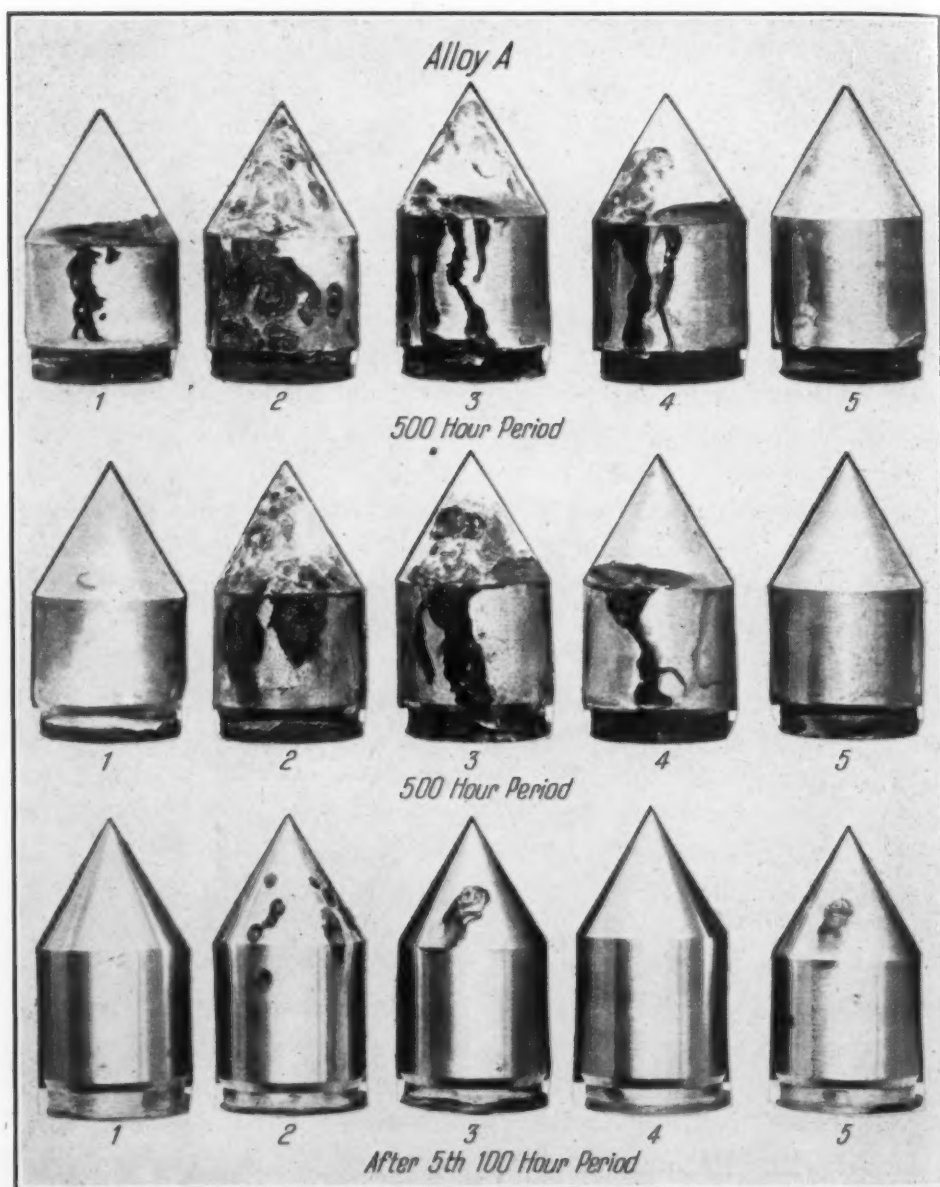
Fig. 2—Alloy A—0.11 Per Cent Carbon, 13.23 Per Cent Chromium after 500-Hour and Five 100-Hour Tests. Serial Numbers Refer to Heat Treatments Shown in Table II.

is hereafter referred to as the 500-hour test; and the other, five 100-hour exposure periods, each period excepting the last followed by cleaning, and referred to as the five 100-hour test. The accompanying photographs illustrate fairly well the rusting which occurred. Figs. 2, 3, 4, 5, 6, 7, 8, 9.

Fig. 3—Alloy B—0.09 Per Cent Carbon, 12.57 Per Cent Chromium, after 500-Hour and Five 100-Hour Tests. Serial Numbers Refer to Heat Treatments Shown in Table II.

Alloys A and B—12.5 Per Cent Chromium—500-Hour Test

Referring to Table II, it will be noted that five different heat treatments are represented, which include a full anneal by slow cooling from above the critical, and four tempering treatments after oil quenching. It has been common experience that a low temperature tempering treatment is unfavorable to rust resistance, and this experi-

Table II

Tabulation of Heat Treatment and Physical Properties

Alloy	Specimen	Heat Treatment	Brinell Hardness	Ultimate Tensile Strength Lbs. per sq. in.	Yield 0.01 In.	Proportional Limit Pounds per sq. in.	Per Cent Elongation in 2 in.	Per Cent Reduction of Area
A	1	1600°F.—25°F. per hour to 800°F.—Air cool	143	71,000	37,500	32,500	37.0	73.5
	2	1750°F., 1 hour, oil; 1000°F., 2 hours, oil	285	117,250	92,500	62,500	24.0	69.3
	3	1750°F., 1 hour, oil; 1100°F., 2 hours, oil	241	105,250	80,000	55,000	25.5	70.4
	4	1750°F., 1 hour, oil; 1200°F., 2 hours, oil	217	97,000	68,750	45,000	27.5	72.3
	5	1750°F., 1 hour, oil; 1300°F., 2 hours, oil	197					
B	1	1600°F.—25°F. per hour to 800°F.—Air cool	137	67,500	35,000	27,500	36.5	69.3
	2	1750°F., 1 hour, oil; 1000°F., 2 hours, oil	285	107,500	87,500	63,500	24.0	70.4
	3	1750°F., 1 hour, oil; 1100°F., 2 hours, oil	235	101,250	80,000	52,500	25.5	72.3
	4	1750°F., 1 hour, oil; 1200°F., 2 hours, oil	217	90,000	62,500	40,000	30.0	75.5
	5	1750°F., 1 hour, oil; 1300°F., 2 hours, oil	189					
C	1	1450°F., 10 hours, water	170	76,250	43,750	27,500	34.5	73.5
	2	1450°F., 10 hours, furnace cool	156	78,000	47,500	37,500	34.5	71.4
D	1	1450°F., 10 hours, water	163	75,750	43,750	30,000	34.5	67.0
	2	1450°F., 10 hours, furnace cool	163	77,500	50,000	40,000	33.5	64.7
E	1	1450°F., 10 hours, water	179	81,750	47,500	40,000	31.0	67.0
	2	1450°F., 10 hours, furnace cool	163	83,000	47,500		32.5	67.0
F	1	1450°F., 10 hours, water	170	74,000	42,500	30,000	34.0	64.7
	2	1525°F., 10 hours, water	170	74,750	40,000	30,000	34.0	62.3
	3	1600°F., 10 hours, water	170	71,750	41,250	30,000	35.0	64.7
	4	1525°F., 10 hours, furnace cool	167	77,500	47,500	40,000	32.0	64.7
G	1	1450°F., 10 hours, water	170	72,750	42,500	32,500	33.5	51.9
	2	1525°F., 10 hours, water	170	74,000	42,500	30,000	32.5	54.7
	3	1600°F., 10 hours, water	179	71,750	42,500	32,500	35.5	59.8
	4	1525°F., 10 hours, furnace cool	163	77,650	50,000	40,000	30.5	58.6
H	1	1500°F., 15 hours, water	170	77,000	52,500	45,000	26.0	57.3
	2	1575°F., 15 hours, water	187	74,250	50,000	40,000	29.0	58.6
	3	1650°F., 15 hours, water	179	68,750	53,750	40,000	3.0	1.9
	4	1575°F., 15 hours, furnace cool	179	70,000	55,000	42,500	2.0	1.9

Fig. 4—Alloy C—0.06 Per Cent Carbon, 17.38 Per Cent Chromium; Alloy D—0.10 Per Cent Carbon, 17.64 Per Cent Chromium; Alloy E—0.15 Per Cent Carbon, 17.21 Per Cent Chromium, after 500-Hour and Five 100-Hour Tests. Serial Numbers Refer to Heat Treatments Shown in Table II.

ence has been confirmed by the present work. The fully annealed specimens and those tempered from 1300 degrees Fahr. showed the best resistance. Some pits have been formed in all samples, but not to a serious or unusual degree. As a matter of fact the more favorably
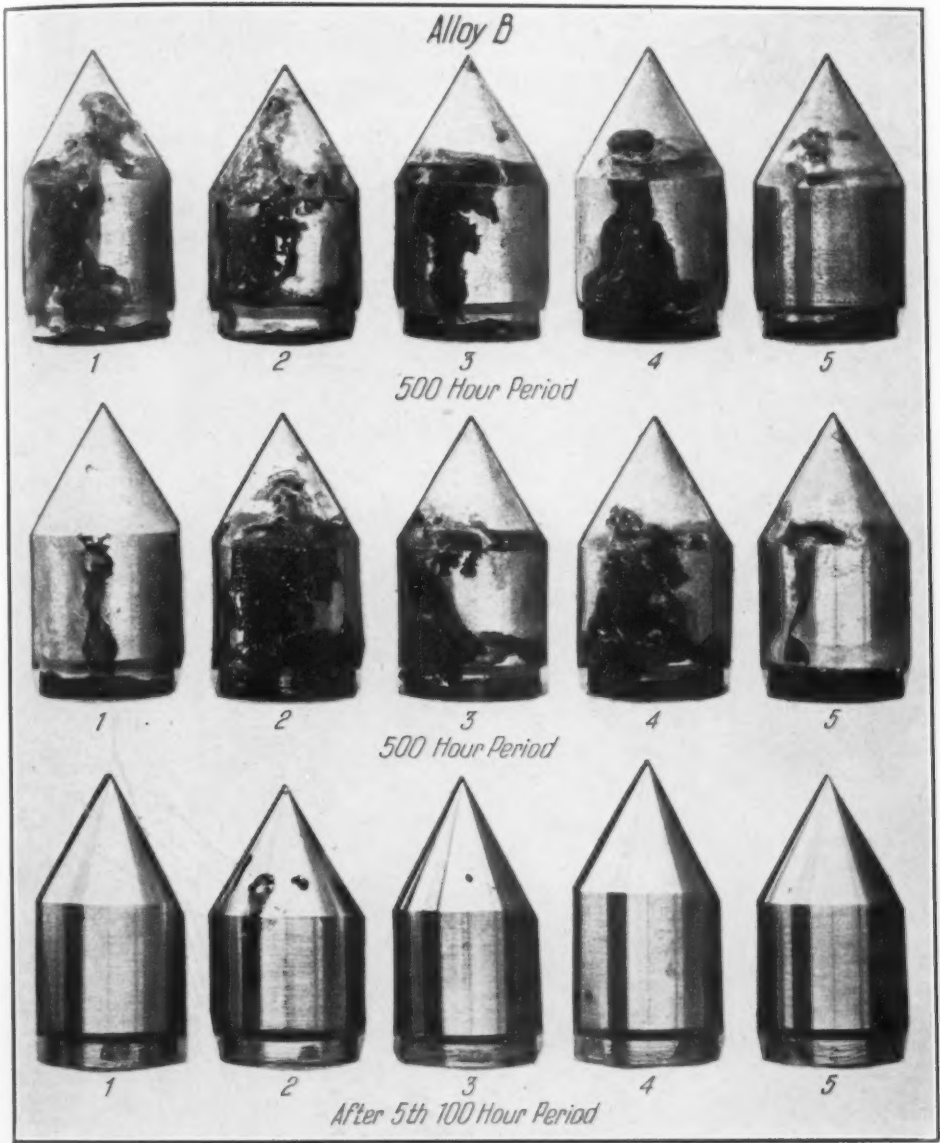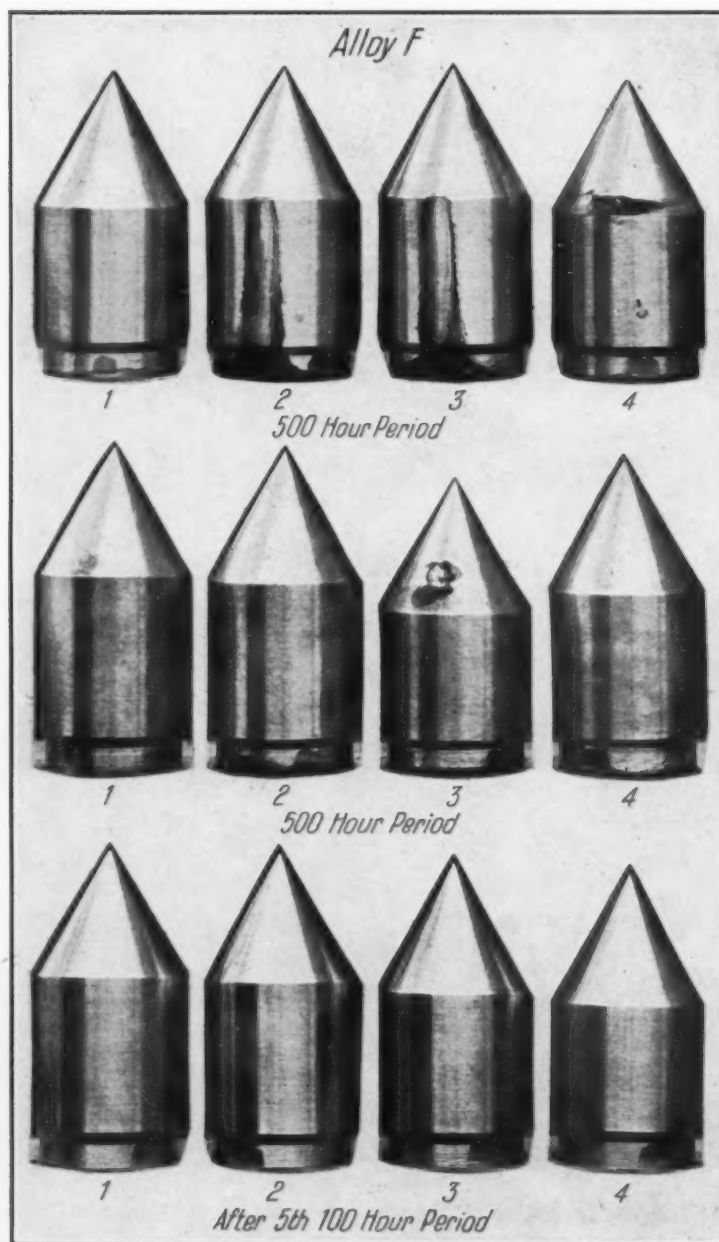
Fig. 5—Alloy F—0.08 Per Cent Carbon, 21.80 Per Cent Chromium, after 500-Hour and Five 100-Hour Tests. Serial Numbers Refer to Heat Treatments Shown in Table II.

heat treated specimens show an unusually good corrosion resistance.

It is interesting to observe (Figs. 2 and 3) that the rust has drained onto the vertical sections of the specimens and made them appear badly corroded in the photographs. As a matter of fact, ex-

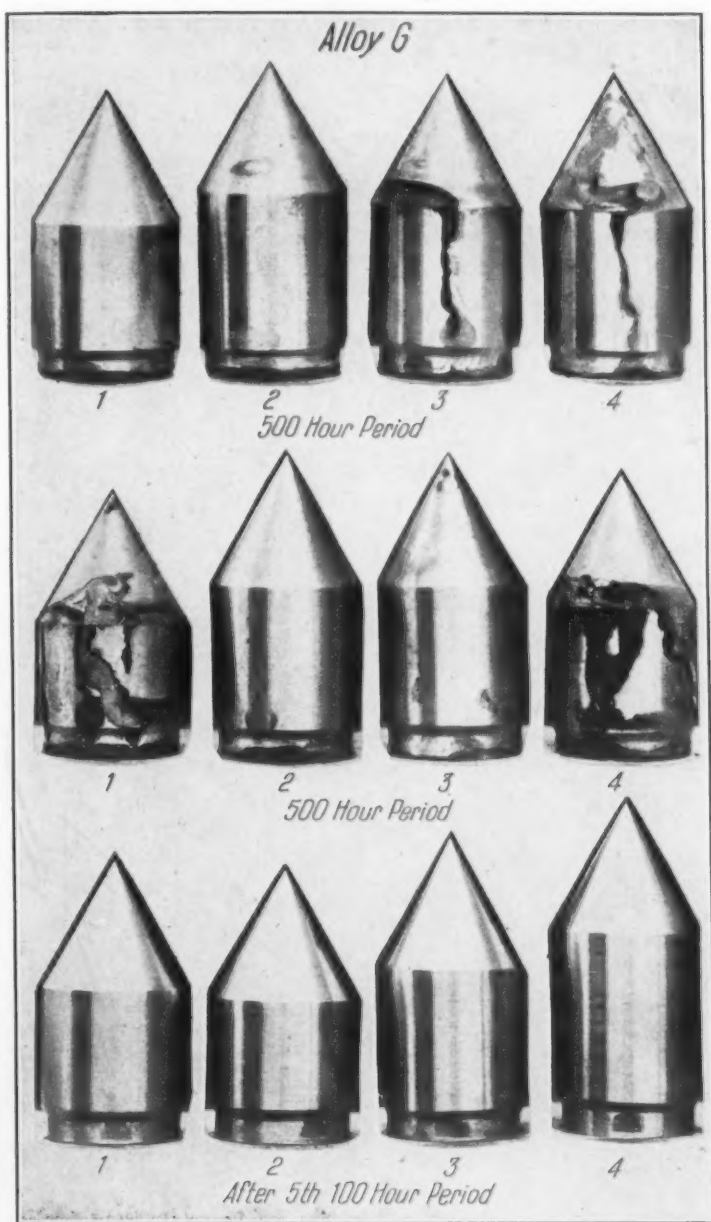Fig. 6—Alloy G—0.13 Per Cent Carbon, 21.49 Per Cent Chromium after 500-Hour and Five 100-Hour Tests. Serial Numbers Refer to Heat Treatments Shown in Table II.

cept perhaps for superficial staining, these vertical sections are entirely unattacked. With this fact clearly in mind, it is evident that most of the rusting occurs on the lower half of the cone. Although it was impossible to determine whether the rate of rusting remained

constant, it was evident that rusting continued to the end of the 500-hour period.

Alloys A and B—13 Per Cent Chromium—Five 100-Hour Test

By referring to the chart (Fig. 10) it will be observed that rusting followed a normal course during the first 100 hours, and that there was a decreasing amount of rusting for each successive period thereafter.

Attention is called to Table III, which lists weight loss figures after each 100-hour exposure period. Although considerable weight loss in milligrams is recorded, especially for Alloy A, the percent-

Table III
Weight Loss During the 5-100 Hour Test

Alloy	Spec-imen	Heat Treatment	Mg. Loss 1st	Salt Spray Test Per 100 Hours 2nd	3rd	4th
A	1	1600°F., 5 hr.—25°F. per hr. to 800°F.—Air	2.0	0.0	0.2	0.0
	2	1750°F., 1 hr., Oil—1000°F., 2 hr., Oil	10.0	5.2	6.2	3.8
	3	1750°F., 1 hr., Oil—1100°F., 2 hr., Oil	6.6	1.8	4.8	0.7
	4	1750°F., 1 hr., Oil—1200°F., 2 hr., Oil	2.2	2.6	2.1	0.0
	5	1750°F., 1 hr., Oil—1300°F., 2 hr., Oil	3.6	1.1	2.1	0.8
B	1	1600°F., 5 hr.—25°F. per hr. to 800°F.—Air	3.2	+1.0	−1.0	0.5
	2	1750°F., 1 hr., Oil—1000°F., 2 hr., Oil	5.8	2.5	5.6	2.7
	3	1750°F., 1 hr., Oil—1100°F., 2 hr., Oil	3.4	0.0	1.7	0.4
	4	1750°F., 1 hr., Oil—1200°F., 2 hr., Oil	1.4	0.1	1.6	0.2
	5	1750°F., 1 hr., Oil—1300°F., 2 hr., Oil	1.9	0.0	0.1	0.0
C	1	1450°F., 10 hours, Water	0.0	0.0	0.0	0.0
	2	1450°F., 10 hours, Furnace	0.2	0.0	0.0	0.0
D	1	1450°F., 10 hours, Water	1.6	0.0	0.0	0.0
	2	1450°F., 10 hours, Furnace	1.4	+0.1	0.0	0.0
E	1	1450°F., 10 hours, Water	0.7	0.0	0.0	0.0
	2	1450°F., 10 hours, Furnace	0.6	0.6	0.0	0.0
F	1	1450°F., 10 hours, Water	0.5	0.0	0.0	0.3
	2	1525°F., 10 hours, Water	1.1	0.0	0.3	0.1
	3	1600°F., 10 hours, Water	0.3	0.0	0.1	0.0
	4	1525°F., 10 hours, Furnace	0.4	0.0	0.0	0.3
G	1	1450°F., 10 hours, Water	1.0	+0.4	−0.4	0.0
	2	1525°F., 10 hours, Water	1.0	+0.6	−0.2	0.0
	3	1600°F., 10 hours, Water	0.0	0.0	−0.7	0.4
	4	1525°F., 10 hours, Furnace	0.6	+0.2	0.0	0.0
H	1	1500°F., 15 hours, Water	0.0	0.0	0.0	0.6
	2	1575°F., 15 hours, Water	0.0	0.0	0.2	0.0
	3	1650°F., 15 hours, Water	0.5	+0.1	0.0	0.3
	4	1575°F., 15 hours, Furnace	0.4	+0.1	0.0	0.0

age loss in terms of specimen weight is very low—approximately 0.001 to 0.01 per cent for the first 100-hour period. Even for the first period all treatments except tempering at 1000 degrees Fahr. result in excellent resistance to progressive and destructive attack. and in all periods after the first the weight losses are negligible.

A comparison of the analyses of Alloys A and B does not suggest that there should be much difference in the resistance to attack

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5.6	2.7
1.7	0.4
1.6	0.2
0.1	0.0
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0.0	0.0
0.0	0.0
0.0	0.3
0.3	0.1
0.1	0.0
0.0	0.3
—0.4	0.0
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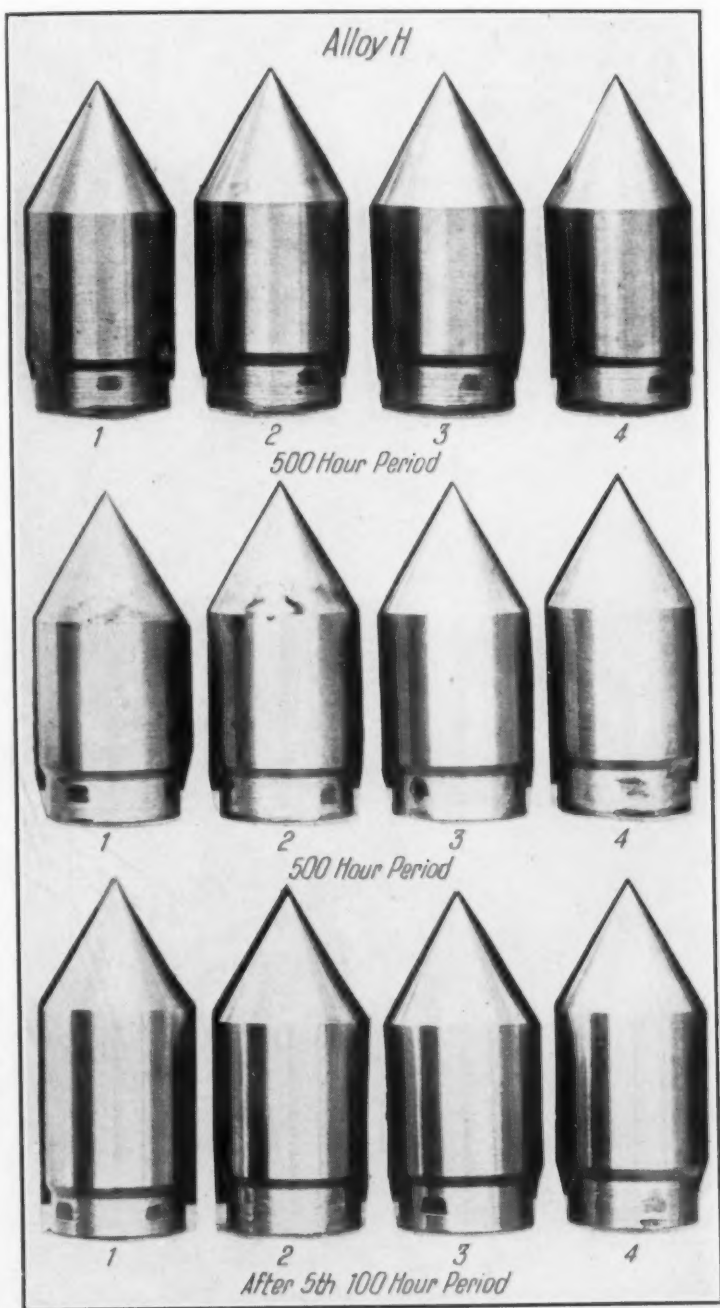
Fig. 7—Alloy H—0.21 Per Cent Carbon, 26.45 Per Cent Chromium, after 500-Hour and Five 100-Hour Tests. Serial Numbers Refer to Heat Treatments Shown in Table II.

on this account. Actually there is very little difference, and after the 1600 degrees Fahr. furnace cool treatment both alloys are equally excellent. This treatment suggests that both alloys were of normal
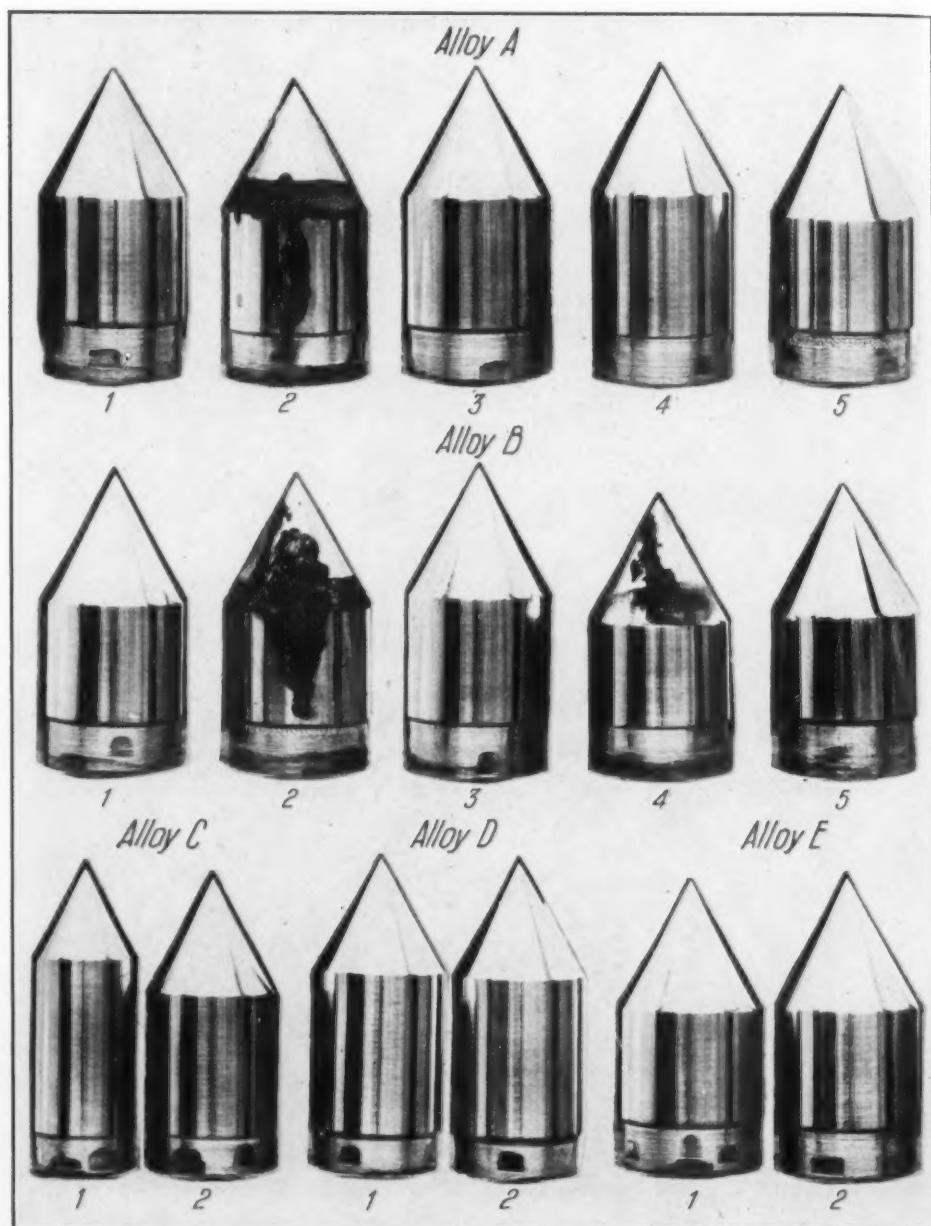
Fig. 8—Alloys A, B, C, D and E.   Polished.   After 100-Hour Test.

quality, and slight differences resulting after the other treatments are most likely due to inconsistencies in the test itself.

Alloys C, D, and E—17 Per Cent Chromium

This group of specimens represents three commercial heats rang-
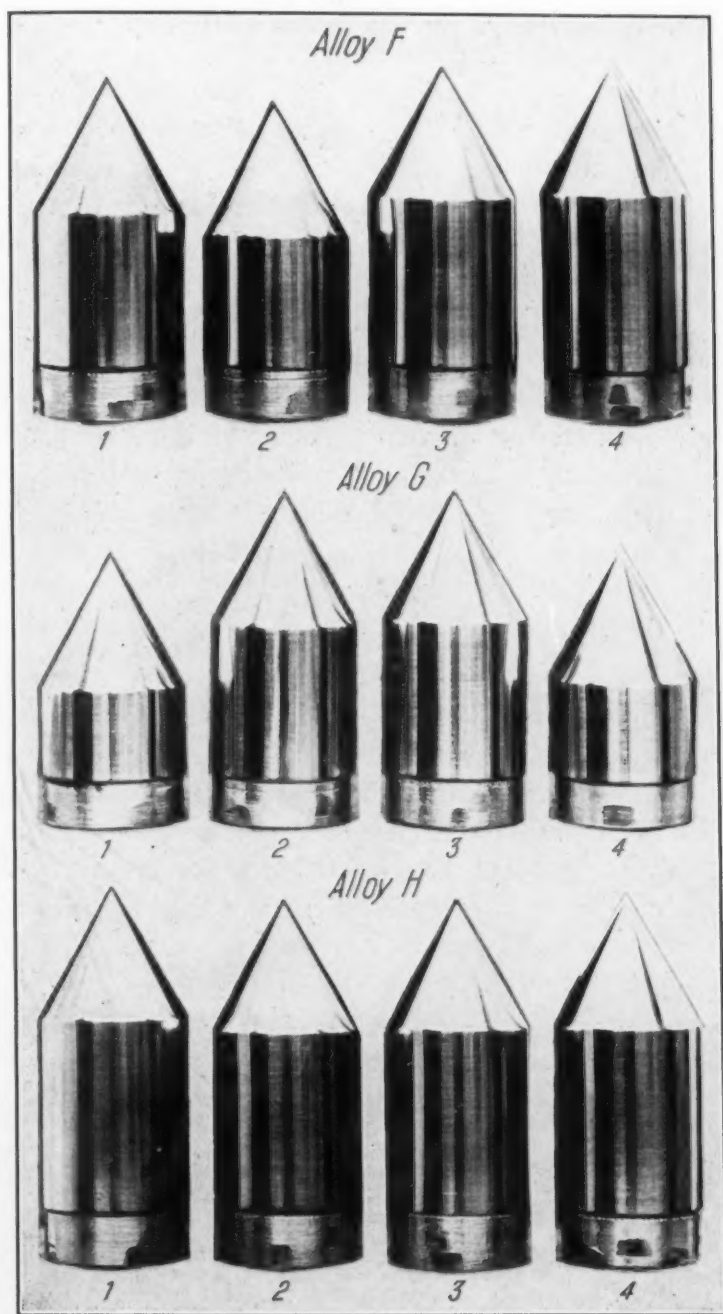
Fig. 9—Alloys F, G and H.   Polished.   After 100-Hour Test.

ing in carbon from 0.06 to 0.15 per cent, and all three containing
about 17 per cent chromium.   The photographs (Fig. 4) illustrating
total rusting after 500 hours exposure are deceptive in that they

suggest a very substantial attack. As a matter of fact rusting was of a very superficial nature and was chiefly confined to the lower parts of the cone sections. There were a few pits, but with a single exception all were so small that their depth could not be measured. The rust adhering to the vertical sides of the specimens had all drained off the cone, and these areas were entirely free of any attack. The deceptive appearance of the specimens was heightened due to the rust being in the form of flocculent iron hydroxide.

By comparison, the five 100-hour test produced slight rusting (Figs. 1 and 4), no pitting, and negligible weight loss. Most of this slight rusting took place in the first 100-hour period. Only faint staining appeared on three of the specimens in the second period and thereafter there was no attack. Variations in heat treatment and analysis did not appear to be significant, the results differing so slightly and in such an irregular manner that there is no apparent relationship.

Alloys F and G—21 Per Cent Chromium

These alloys are similar in behavior to the ones containing 17 per cent chromium (Figs. 5 and 6). The only rusting which occurred is superficial surface staining without any well developed pitting. In the five 100-hour test the appearance and weight loss figures show excellent and equal resistance for both alloys despite considerable difference in carbon content and heat treatment.

Alloy H—26.5 Per Cent Chromium

This grade of rustless iron is not ordinarily employed for atmospheric or salt water resistance, and for these reasons fewer data have been accumulated bearing on its rust resisting qualities. Therefore, samples were included, and as might be expected, showed practically perfect resistance (Fig. 7). Only the faintest surface staining was discernible even after 500 hours continuous exposure. In the five 100-hour test, staining was so slight and weight loss so small as to be negligible.

DISCUSSION

In reviewing the test results, the difficulty in judging or comparing the rust resistance of the various specimens becomes at once evident. A large quantity of iron hydroxide rust is formed from

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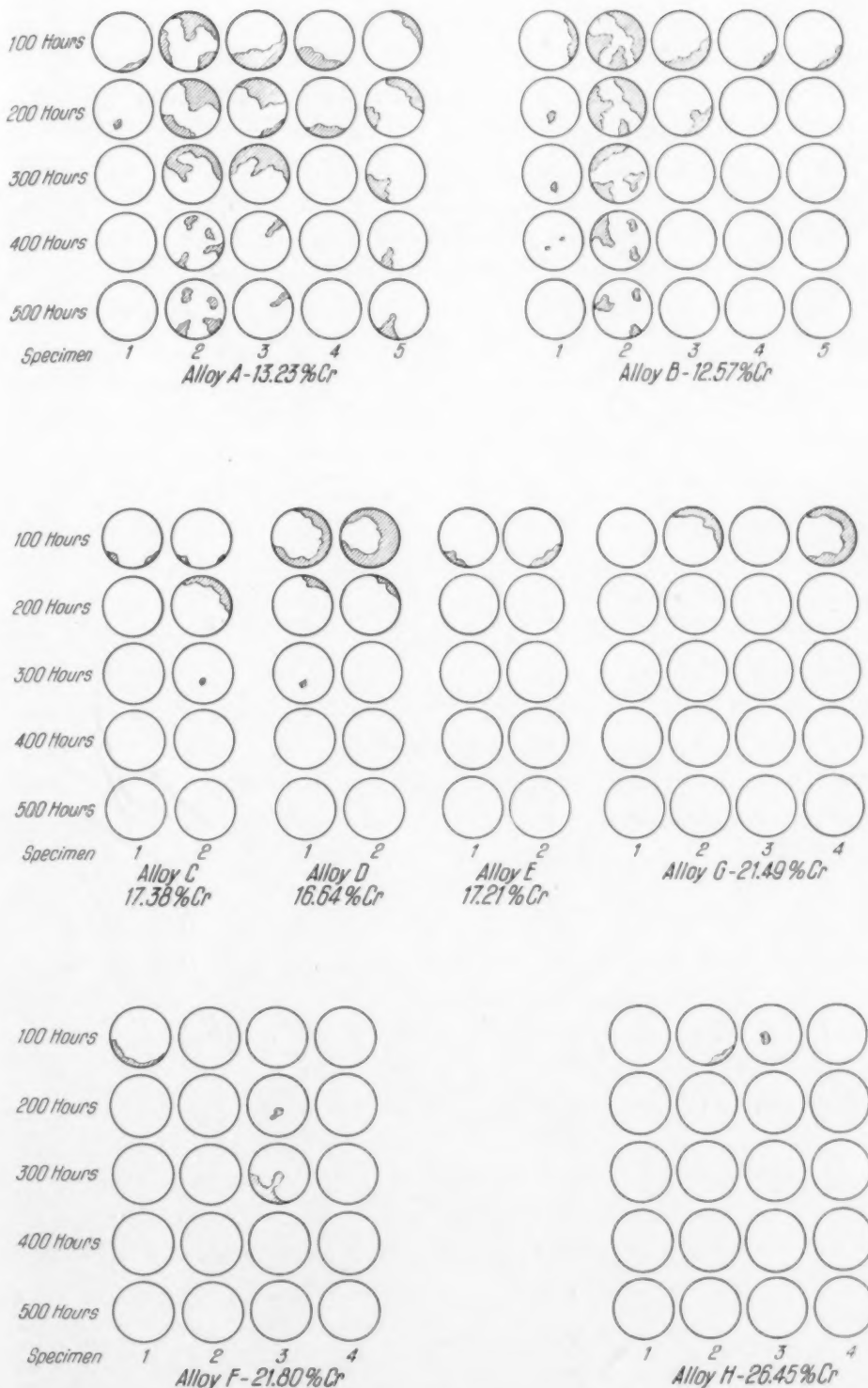
Fig. 10—Chart Showing Appearance of Specimens after Each 100-Hour Period. Cleaned Before Re-exposing.

the most minute staining or pitting. The appearance of the exposed samples is no criterion of their rust resistance until after the adhering rust has been sufficiently removed to permit inspection for pits or other local attack. For instance, the rust which adheres to the vertical sides is by no means an indication of attack—on the contrary it is evidence of an entirely different characteristic which could best be described as a tendency to collect or precipitate out of the solution the rust which drains down off the cones of the specimens. The same is equally true of the cone; the rusted spot is always larger than the attacked area. It was apparent that some of the 13 per cent chromium specimens did exhibit clearly developed pitting, and therefore progressive attack. And a few of the specimens containing 17 per cent chromium also showed a suggestion of progressive attack in the form of incipient pits after 500 hours exposure. All other specimens showed more or less staining after 500 hours, but no well developed pits. When an effort was made to measure quantitatively the amount of attack practically all of the weight loss figures were so small as to be within the limits of experimental error. In view of the rough surfaces of the specimens and the long duration of the tests, considerable satisfaction was felt at the excellent rust resistance shown by all of the alloys.

It is unfortunate that a parallel series of cold-rolled annealed strip specimens was not included in the investigation. Considerable amounts of strip are made from the 17 per cent chromium alloys, much of which is used in the cold-rolled, annealed and polished condition as for instance for automobile trim, and in this condition its resistance to rusting is uniformly excellent over considerable periods of time. Even when strip is unpolished it is seriously suggested that the effect on its structure and surface of the cold rolling operation may induce resistance to the salt spray and to ordinary rusting which is superior to the resistance of bar stock, machined and smoothed, but unpolished, such as was used in this investigation. There is some basis for this belief when it is realized that specimens of commercial unpolished strip containing approximately 0.10 per cent carbon and 17 per cent chromium have actually been subjected to a 1000-hour salt spray test (4 per cent sodium chloride solution) without showing any signs of attack.

However, a fairly representative group of analyses were included among the specimens investigated, and the heats themselves were

used commercially without any failures on account of corrosion or physical defects. Also it has been frequently observed that other heats of similar analysis, even in bar form, showed no trace of rusting or staining when exposed for 100 hours in the salt spray. In contrast to this kind of performance, a considerable proportion of these specimens, in all grades, showed more or less rusting or staining, which in a good many instances showed up in the first 100 hours. Although this slight degree of rusting was not surprising when it was considered that the exposed surfaces were unpolished and unpassivated, it was realized that some supporting evidence must be offered before concluding that these specimens would have been fully equal in resistance to previously tested material if they had been polished.

Therefore, the specimens comprising one of the two sets which had been exposed continuously for 500 hours were cut down slightly in size and dry polished, finishing with No. 000 Behr Manning papers. The emery on these papers contained about 35 per cent Fe_3O_4. These polished specimens were then exposed for 100 hours. Inspection revealed that all were entirely free of staining or rusting except two 13 per cent chromium specimens which had been tempered at 1000 degrees Fahr. and one at 1200 degrees Fahr., and these showed only superficial rusting (Figs. 8 and 9).

A further check on the normal corrosion resistance of the specimens was made by selecting several from the five 100-hour set and submitting to the boiling nitric acid test for two 50-hour periods. For this purpose, disks were machined from the salt spray specimens which were about $3/8$ inches thick and slightly less in diameter than the original diameter of the salt spray specimens. The results of this check test are shown in Table IV.

Examination of these results does not reveal any serious divergence from normal. The attack on Alloy B (1750 degrees Fahr. oil, 1300 degrees Fahr. oil) during the first period is slightly high, but diminishes to normal in the second period. The rate for Alloy C (0.06 carbon, 17 per cent chromium) is slightly high, but it must be kept in mind that this test is affected by heat treatment up to at least a 20 per cent chromium content of the alloy, and that the treatments given to these specimens differed somewhat from ordinary practice. Indeed, considering the low carbon content and the low temperature treatment it is very probable that the spheroidizing of the carbides has not been completed despite the long soaking period. At any rate it will be recalled that Alloy D of this group (0.10 per cent

Table IV
Rate of Attack in Boiling Nitric Acid Test

Alloy	Spec- imen	Heat Treatment	Nitric Acid Test Inches pen. 1st 50 hrs.	per month 2nd 50 hrs.
A	1	1600°F.— 5 hr., 25° per hr. to 800°F.—Air	0.01300	0.02160
	5	1750°F.— 1 hr., Oil—1300°F., 2 hr., Oil	0.01257	0.01850
B	1	1600°F.— 5 hr., 25° per hr. to 800°F.—Air	0.01340	0.01950
	5	1750°F.— 1 hr., Oil—1300°F., 2 hr., Oil	0.02040	0.01590
C	1	1450°F.—10 hours—Water	0.00217	0.00307
	2	1450°F.—10 hours—Furnace	0.00253	0.00272
D	1	1450°F.—10 hours—Water	0.00176	0.00182
	2	1450°F.—10 hours—Furnace	0.00177	0.00211
E	1	1450°F.—10 hours—Water	0.00226	0.00237
	2	1450°F.—10 hours—Furnace	0.00244	0.00266
F	2	1525°F.—10 hours—Water	0.00121	0.00130
	4	1525°F.—10 hours—Furnace	0.00116	0.00113
G	2	1525°F.—10 hours—Water	0.00108	0.00106
	4	1525°F.—10 hours—Furnace	0.00076	0.00099
H	2	1575°F.—15 hours—Water	0.00136	0.00193
	4	1575°F.—15 hours—Furnace	0.00129	0.00163

carbon) exhibited slightly more rusting in the salt spray test than the other two, whereas its nitric acid rate is the best.

In line with these check tests, the tensile test results (Table II) were carefully examined for signs of abnormal characteristics. Minor discrepancies where they occur are readily understandable in view of the heat treatments selected and the normal variation between tensile bars. For instance Alloy H develops characteristic brittleness after two of the treatments, emphasizing that the treatment is not correct.

In the light of these considerations, there is little doubt that the alloys were of normal quality, and that the test results should represent normal expectancy for the alloy types investigated. Moreover, it is evident that all of the alloys studied are inherently resistant in the salt spray test. Only a few showed even slow progressive rusting after 500 hours exposure. All might reasonably be expected to withstand progressive attack due to atmospheric exposure for an indefinitely long period in commercial use, and certainly all of the alloys containing 17 per cent or more of chromium should be equally satisfactory for marine service. If service conditions should provide satisfactory drainage or permit occasional wiping, complete freedom from progressive attack might be expected of all the alloys. Wherever the exposed surfaces are to be polished a satisfactory margin of safety is provided.

The effect of heat treatment on the resistance of the 13 per cent chromium alloys is well known, and need not be discussed here, except to record that the behavior of the investigated specimens was normal. There is no reason to believe that the long time treatments

Acid Test
per month
2nd 50 hrs.
0.02160
0.01850
0.01950
0.01590
0.00307
0.00272
0.00182
0.00211
0.00237
0.00266
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selected for all samples containing 17 per cent or more of chromium were helpful. In some cases the treatment suited the alloy, in others it did not. Previous experience indicated that the salt spray test is not particularly sensitive to the effect of minor variations in heat treatment, and this investigation confirms these findings. Of course, this conclusion must be qualified, for up to at least 20 per cent chromium content it is known that hot-rolled material, welded seams, or grossly overheated metal is more susceptible to attack due to these inadequate or unsuitable treatments.

Consideration of the effect of analysis on salt spray resistance has led to only a few generally familiar conclusions. It is obvious that the resistance of the alloys improves with increasing chromium content. For all ordinary service requirements which permit favorable heat treatment and a smooth finish, it would seem that 17 per cent or 18 per cent chromium content in the alloy is sufficient, and this is particularly true if condensation or drainage of moisture or salt water on the metal does not occur; or in case it does, if occasional wiping is permitted. Likewise, the effect of local test conditions such as heat treatment, surface finish, shape of the specimen, oxide film, etc., decreases with increasing chromium content. Presence of a high carbon content within the limits represented by the materials investigated is not shown to be serious, and previous experience has taught that when such alloys are properly heat treated they are substantially equal in corrosion resistance to similar alloys with low carbon. The principal usefulness of the iron-chromium alloys containing more than about 20 per cent chromium lies in other fields, such as that of heat resistance, and the investigation has indicated that their rust resistance is more than sufficient for atmospheric conditions or marine service.

Other factors, such as the effect of large nonmetallics which may protrude at the exposed surface, or of chemical heterogeneity, have not been studied in this investigation. Since all rustless iron heats produced at the plant where these tests were conducted are made according to an established and carefully controlled practice, it is rare indeed that a heat is not commercially clean, sound, and dense, and of satisfactory quality for commercial use. Also it has frequently been observed that the free-cutting types of rustless iron, both 13 per cent chromium and 18 per cent chromium-8 per cent nickel, possess excellent salt spray resistance. If nonmetallics tend to break down rust resistance certainly the abundance of sulphides present in these

grades should seriously affect their resistance. As for segregation, rustless iron is "thick" when molten, and although it has a fairly wide solidification range it is rarely observed that serious chemical heterogeneity exists. The evidence so far discussed does not adequately account for the behavior of these alloys, especially when the results after continuous exposure (in the 500-hour test) are contrasted with the results after interrupted exposure (in the five 100-hour test). Continuous exposure evidently causes very slow, but continuous attack on one or more specimens of every alloy tested, which frequently commences during the first 100 hours. In some cases this attack leads to pitting or incipient pitting, and promises a variable slow rate of progressive corrosion in the course of time. In contrast to this behavior it was equally clear that the five 100-hour test did not induce continuous attack. In fact, rusting started in a normal manner during the first 100-hour period, but thereafter in succeeding periods it decreased to zero. It was also observed in both tests that the vertical sides of the specimens were virtually immune to attack, and that in most instances the only areas attacked were in the lower sections of the conical surfaces. These observations support the indisputable findings of many investigators and users of these alloys that the preparation of the exposed surfaces is exceedingly important in determining their resistance to the salt spray and to general rusting. Of course, in view of the electrochemical nature of rusting, the importance of the exposed surfaces is not surprising. Indeed, it is not possible to find an explanation of the process of rusting without resorting to the principles of electrochemistry.

Considerable evidence has been accumulated in support of the view that iron-chromium alloys depend on a thin invisible oxide surface film for protection against rusting, or other oxidizing corrosive attack. This film is probably not more than a few molecules thick. It is formed quite rapidly, even under such mild oxidizing conditions as atmospheric exposure. If this oxide film is continuous, and impervious to penetration by oxidizing reagents, it is natural that the underlying metal would be perfectly protected against attack, as for instance rusting. However, according to Evans[7], the chloride ions of a salt solution possess the ability to penetrate or destroy the oxide film, so that even though the film might be continuous it would still

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[7]U. R. Evans, "Corrosion of Metals," 2nd Edition, Edward Arnold & Co., (London), 1926.

be possible for galvanic attack to proceed at any points where the film was too thin to serve as an effective barrier against the electrolyte.

It would appear reasonable that freshly prepared specimens having rough unpolished surfaces might afford opportunity for collecting droplets of solution before an adequate oxide film had formed. Of course, the salt spray itself is quite thoroughly aerated, and there is an abundance of air in the chamber, so that the condition should be oxidizing. But this does not mean that all parts of the specimens are exposed to a uniform oxidizing action. On the contrary, it is quite likely that those areas of the specimens covered by droplets of solution are to some extent protected against oxidation such as would build up the surface film. This point is significant when it is considered that drainage of the spray droplets off the cone sections of the specimens is usually quite slow, and very ununiform. Due, no doubt, to minute irregularities in the surface contour of the specimens, the droplets were in some cases very tiny, in others quite large, and in all there was a tendency for solution to collect around the bottoms of the cones. These tiny pools of solution, held in place by capillary action, would sometimes hang on one side and extend some distance upward, or they might form rings extending all or part way around the specimens. This condition developed very quickly and persisted throughout the duration of the tests.

Since freshly aerated mist is constantly being added to the outer surfaces and edges of these droplets, there should be a higher oxygen content in these outer surfaces. As shown by Evans[7] this circumstance permits formation of a galvanic cell, the anode of which is at some point where the oxide film is broken, or where the chloride ions have succeeded in penetrating the film. The cathode of this cell may be any surrounding point or area where there is a ready replenishment of the oxygen content of the solution. Sodium hydroxide and hydrogen are formed at the cathode, and the hydrogen combines with the available dissolved oxygen. At the anode soluble iron chloride is formed and this product disseminates through the solution until it meets with sodium hydroxide whereupon flocculent ferrous hydroxide is formed.

These reactions depend for their continuance on a constant supply of oxygen at the cathode. The potential in such a cell is not great enough to liberate molecular hydrogen, and without a constant supply of oxygen to combine with the atomic hydrogen formed, the cathode will be blanketed or polarized, and the current will cease to flow.

This oxygen is supplied in abundance by the fresh spray and air constantly passing through the chamber, and it is supplied first to the cathodic areas. It is probable that the solution in contact with the anodic point of the cell has been rendered somewhat deficient in oxygen by the constant demands for oxygen of the cathodic reaction. It is possible that the oxygen available at the anode, whatever the amount may be, is constantly repairing the oxide film, and thereby retarding the inroads of corrosion, but it is evident that this reaction would proceed under difficulties, and might fail to halt the corrosive attack. The same reaction can proceed when water or moisture is substituted for the salt solution, but of course corrosion is not so active nor does it proceed rapidly.

If an electrochemical action of this kind is once started it might be expected to proceed indefinitely, and its progress will be rapid or slow depending on local conditions such as shape or dimensions of the cell, rapidity of drainage, etc.

It will be remembered that one set of specimens was removed from the salt spray after 100 hours, cleaned, and re-exposed. This procedure evidently permitted repair of the oxide film at points which had proven defective in the first period. If the attack proceeded in the manner outlined, it is natural that there should be little or no attack in the second period. That this actually was the case is amply demonstrated by the chart in Fig. 10.

It may well be that other considerations aside from oxide film and galvanic action are involved. Perhaps the facility with which the oxide film forms may be governed by some factor involving the quality of the metal. However, it does not seem now that the significance of electrochemical attack has been over-emphasized. Other investigators have had similar experience in studying the mechanism of rusting. For instance, Evans[8] has obtained time-potential measurements for iron and steel in a tenth molar potassium chloride solution. He found there was a low initial potential which rapidly fell to —0.4 volts. Iron-chromium alloys containing about 13 per cent chromium showed higher initial potentials which fell off to about —0.2 volts. Quoting Evans directly, "Alloys of higher chromium content showed distinctly higher values, and in spite of some irregularities in the early stages, doubtless due to local breakdown and subsequent repair, maintained these values well." Similarly, Raw-

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[8]Bannister & Evans, "Passivity of Metals, Part V," *Journal*, Chemical Society, June, 1930, p. 1361.

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don, Grossmann, and Finn[9] found that samples of galvanized sheet placed vertically in the salt spray were more rapidly corroded than when inclined or placed horizontally, and that the zinc coating was least rapidly destroyed when the sample was totally immersed. These experiences do not exactly parallel ours, but they do bear witness to the importance of seemingly minor factors, and to the complexity of corrosion problems.

The final point in our discussion is a brief consideration of the value of the salt spray test. It has little commercial value unless it gives some indication of the probable service performance of the tested materials.   Since it appears that behavior during test is influenced not only by the inherent rust resistance of the alloy, but also by entirely unrelated factors, some of which may not be experienced in the field, it is necessary for the investigator to carefully weigh the importance of the results obtained through the influence of these outside factors.   After all, the chief function of the test lies in attempting to compare the resistance of a number of similar alloys in standard equipment but under purely artificial and severe conditions. When sufficient specimens have been investigated, much experience is gained, and the average behavior of the alloy may be observed.   The interpretation of the salt spray test, however, is not so simple that a correct parallel may be drawn between performance in the test and performance in service.   Intimate knowledge of service conditions must be had, and a background of experience with the same or similar alloys in like applications must be drawn upon.

Certainly if a representative group of specimens is entirely free from attack in the salt spray, it is safe to assume that the particular alloy tested, similarly heat treated and prepared, should be indefinitely resistant to attack in the atmosphere or in marine service.   If staining or progressive attack occurs in the salt spray, interpretation of the test results in terms of service performance must depend on the investigator's judgment and previous experience, and on the service requirements.   This is not always a difficult matter, because wide experience with all of the alloys tested has proven that without exception they are highly resistant to corrosion for ordinary applications, and it is only in cases of unusual and severe conditions that there is serious chance for misapplication.

As an indicator of general corrosion resistance it does not seem

[9] loc. cit.

that the salt spray test is satisfactory. Often it is not sufficiently sensitive to discern differences in heat treatment, and it makes no attempt to measure the effect of temperature variations. Because results depend quite largely on such superficial factors as preparation of the surface and condition of the invisible oxide film, the results are not consistently reproducible.

Although the authors freely acknowledge the usefulness of the salt spray test, they also feel that it has many disadvantages, some of which could probably be remedied. To this end it is desired to direct special attention to the following factors, most of which undoubtedly have some effect on the nature and degree of attack in the test.

a. Number of specimens required in order to obtain representative results
b. Size and shape of specimen
c. Preparation of the surface
d. Position in the spray chamber
e. Duration of the exposure period
f. Time elapsing between preparing the specimens and exposing them
g. Use of iron-containing compounds for polishing or smoothing of the surface
h. Advisability of intermittent exposure (such as the five 100-hour test) with cleaning of the specimens after each exposure period
i. Temperature within the spray chamber
j. Most suitable concentration of the salt solution
k. Suitability of the salt (sodium chloride or sea salt) solution
l. Possibility of combining immersion or partial immersion test with the spray test
m. Passivation before exposure.

CONCLUSIONS

The following conclusions may be drawn.

1. The alloys tested, ranging from 13 to 26.5 per cent chromium, and including specimens having unpolished as well as polished surfaces, all possess excellent resistance to rusting in the salt spray test.

2. No direct parallel can be drawn between resistance in the salt spray test and rust resistance under service conditions.

3. The salt spray test cannot be used to express a direct measure of general corrosion resistance, as for instance, to predict from its results what might be expected from the alloy in resistance to an acid.

4. The salt spray test is not very sensitive to differences in analysis, although there is considerable improvement in resistance when the chromium content is increased from 13 to approximately 17 per cent. Above 17 per cent chromium there is slight improvement in the case of unpolished specimens, but it is believed that 17 per cent chromium offers adequate resistance so that the higher chromium alloys would not ordinarily be required for rust resisting applications.

5. The effect of removing the products of corrosion after a period of exposure in the salt spray test, is to improve the resistance of the specimen to subsequent exposure. This observation held true for all specimens, both high and low chromium, and in most cases, a single cleaning served to reduce subsequent attack to zero.

6. The salt spray test is not very sensitive to differences in heat treatment when the chromium content is 17 per cent or more.

7. Within the limits studied, differences in carbon content do not appear to have any marked effect on resistance to attack.

8. The shape of the specimen has an effect on salt spray resistance.

9. Since the alloys tested were of good commercial quality according to the usual criteria of quality, such as structure, nonmetallic content, etch tests, etc., it does not appear that these common tests can be used to account completely for salt spray and general rust resistance.

10. Preparation of the exposed surfaces is important in influencing resistance to the salt spray. A highly polished surface is most resistant. Of the alloys here investigated, polished specimens containing 17 per cent or more chromium were immune to attack after 100 hours of continuous exposure; alloys containing approximately 13 per cent chromium were attacked only in three instances, and the degree of attack was slight.

ACKNOWLEDGMENT

Iron Corporation of America, who furnished the rustless iron materials required for the investigation, and who gave permission to publish the results of this work which was done directly in behalf of the Rustless Iron Corporation of America. Messrs. H. S. Schaufus and S. P. Watkins, metallurgists of the Alloy Research Corporation, gave much valuable assistance in the preparation and heat treatment of the samples, and to them many thanks are due.

DISCUSSION

Written Discussion: By V. N. Krivobok, associate professor of metallurgy, Carnegie Institute of Technology, Pittsburgh.

The general impression one gets upon reading the paper under discussion, is the comprehensiveness of the work undertaken, and the critical attitude of the authors toward the methods employed and the results achieved. At the beginning of this commendable presentation the authors summarize the purpose of the work they have accomplished as follows: "to call attention to some of the peculiarities and to the noninfallibility of the salt spray test and to the resultant complications when using this testing method as an index to the behavior of the alloys in service; also, to instigate a more critical scrutiny of the salt spray test in the hope that better standard methods for making the test might be worked out." The results of the investigation, as set forth, and as presented, prove that the authors have fulfilled their promise. Upon reading this carefully conducted investigation, even if one has not had experience with the salt spray test, one would readily agree with the authors that the salt spray test must be conducted with especial care and intelligence. That the salt spray test is useful and, at present, the most indicative, no one thoroughly familiar with it would deny. But at the same time it is not an infallible test, and consequently, its reliability should not be looked upon as dogmatic. This must be constantly borne in mind, especially when the results of the test are discouraging, or in disagreement. The complexity of various factors entering into this problem are well presented by the authors and, if I may, I would like to suggest that the conclusions at which they arrived should be kept on the desk of every one concerned with this phase of metallurgy. It may be further suggested that in conducting the salt spray test the actual service to which the alloy in question is to be subjected should be kept in mind. For it is obvious, as the authors prove, that there is no such alloy as could be termed "noncorrosive," if tarnishing, (or slight rusting, easily removed) is made a criterion of either "corrosive" or "noncorrosive" alloys.

It was with much interest that I read the assertion of the authors that the chromium alloys containing, in general, approximately 13 per cent chromium should be subjected to carefully conducted heat treatment. Also, that above 16 per cent chromium the effect of the heat treatment is not so marked and that with still higher chromium content "over-heating resulting in coarsened grain, and concentration of carbides along grain boundaries reduces the resistance of the alloy." A natural question arises whether the same holds true in

case of 13 per cent chromium since it is known alloys of this composition if over-heated may develop large grain size. In other words, the studies of the temperature of the heat treatment interpreted in terms of structural conditions versus resultant corrosion resistance, and conducted as carefully as the work presented in the paper will be very timely.

The authors state that iron-chromium alloys above 16 per cent chromium are extremely sluggish in reacting to heat treatment, (page 433). The meaning of the expression "heat treatment" is not quite clear to me, and if it implies the improved homogeneity of the alloy after the heat treatment, I do not agree with the authors on placing chromium content at 16 per cent, since from experience I find that in all chromium alloys of over approximately 6 per cent chromium, chemical homogeneity is attained with much difficulty. I would also refrain from stating that the long time treatments would result in bringing about an equilibrium. I permit myself to offer this suggestion because I fully agree with the authors that the homogenizing treatment with a tendency toward improved equilibrium not only might be but most probably is a factor in salt spray resistance.

The abolition of very fine polishing of the samples during the course of the investigation should be especially commended. I believe that every one would agree with the authors that the purpose of the salt spray test is to determine the inherent resistance of the metal to corrosion rather than superficial resistance brought about by a highly polished surface. In other words anything that would tend to screen the difference in quality, heat treatment, and analysis should be carefully avoided.

It is to be noted that besides comprehensive treatment of the question of the salt spray test the paper also contains other valuable information. Very interesting data on mechanical properties of the alloys are included in Table II. As will be observed, in this table are gathered the results of mechanical tests on the alloys for all practical purposes identical in composition except for the carbon content. The results on the alloys with 17 per cent chromium are particularly interesting and show that the carbon content has practically no influence on the mechanical properties under the conditions of treatment as stated in the table. The comparison of this table with the data on salt spray corrosion is interesting.

I was much interested, and I must confess stimulated, by the authors' statement that low temperature tempering treatment is unfavorable to rust resistance. Recently, an investigation was completed in the laboratories of Carnegie Institute of Technology by Lt. Holderness, U. S. N., and Lt. France, U. S. N.,* such investigation being undertaken to check on the assertion that chromium alloys of 13 per cent and 17 per cent chromium show a very marked decrease in resistance to impact after drawing between 900 and 1000 degrees Fahr. Carefully conducted microscopic examination has failed to clear the matter, although the indications were that the disintegration of the material with subsequent separation of carbides is most probably responsible for this phenomenon. It is quite natural to ask whether the phenomenon of increased

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*Holderness and France, "Effect of Heat Treatment on Properties of Stainless Steel." A thesis presented to Carnegie Institute of Technology.

brittleness after low temperature draw and the lessened resistance to corrosion are not closely affiliated.

Referring to the authors' theoretical discussion of the subject, it is indeed difficult to refute their statements, even if one had the desire to do so, in the absence of more precise and detailed knowledge, as the authors themselves point out. It may be easily admitted that the problems of corrosion are just as complex as the problems of deterioration. Those who fail to see the complexity of the problem might well read the recent Edgar Marburg lecture** by Dr. Hugh S. Taylor in which the nature of the reactions involved and the probabilities of various, and oftime unsuspected, influences with the resultant errors in deductions are clearly stated. The lecture is a theoretical treatise.

The authors of this paper have given us a very cautiously prepared and frankly worded manuscript on the actual observations thoughtfully and carefully obtained. In their next publication one will expect to find further answers to the perplexing question of corrodibility.

F. N. SPELLER:[1] It seems to me that the impression might be gained that this test can be used in a much broader sense than many of us believe is possible. In fact, that applies to any one test.

There is no one yardstick, of course, for rating corrosion. The authors have well brought out the limitations in one respect of this salt spray test and the need of standardizing it.

Report of Committee B-3 of the A. S. T. M., on Corrosion of Nonferrous Metals and Alloys, 1932, page 9, contains a comprehensive analysis of the salt spray test based on a thorough investigation made by this committee. They point out the advantages and limitations of this method of test. Obviously, the test does not give reliable information of the resistance of the metal to various solutions when the specimens are continuously immersed.

I wish to take this opportunity to congratulate the authors on the very thorough way in which they have treated the subject.

A. C. JONES:[2] I would like to ask the authors whether they have found a passivating effect from the air on any of these stainless steels following machining or polishing, as the result of letting them stand for a relatively long period before subjecting them to the salt spray or other corrosion conditions. If so, how does this effect compare with that obtained in nitric acid?

F. R. PALMER:[3] One could not help but feel, in listening to this paper, how fairly the authors had discussed the subject of salt spray testing. It would not seem to require any supplementary remarks excepting that so often we find the salt spray test is employed in just the way that they recommend it should not be. For one thing we find it used as though it were an exact measuring instrument like a micrometer, which it is not. If I were to liken the salt spray

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**Hugh S. Taylor, "Fundamentals in the Problem of Resistance to Determination." Edgar Marburg Lecture read on June 22, 1932, before American Society for Testing Materials. Preprint, Vol. 32, Part, II, 1932.

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[1]National Tube Co., Pittsburgh.

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[2]Metallurgist, Lebanon Steel Foundry, Lebanon, Pa.

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[3]Carpenter Steel Co., Reading, Pa.

test to some piece of testing equipment, I should say it is more like a snap gage. A snap gage does not mean anything at all until you have identified the dimensions of it, established some limits for "go" and "no go," and then your gage begins to mean something as a test. That is the way the salt spray test should be used.

We should not attempt to subject steel to a salt spray test until we find out what degree of resistance in a salt spray test is necessary for work in our particular service. The Navy Department has established this method. They do not ask for perfection in salt spray testing. They have a series of degrees of attack, A, B, C, and so on. They have established by actual test that certain degrees of resistance are necessary for certain purposes. If the steel falls below that degree in their salt spray testing, they reject it, and if it meets that limit they accept it.

In other words, they set their salt spray test gage to the requirements, but they do not try to determine by the salt spray test whether the material is okay for the purpose. After having determined what degree of corrosion resistance the job requires, they test a material that meets these requirements in the salt spray and thereafter they expect subsequent material to come up to that standard.

To illustrate further, I have in mind a case where 14 per cent chromium stainless iron was being tested for parts in a certain piece of apparatus that was expected to withstand ordinary atmospheric corrosion. No effort was made to find out whether the steel was satisfactory for the purpose intended. It was put in a salt spray test and was rejected because it did not show perfect resistance.

They had been using a nonferrous alloy for corrosion resistance and finally, to get some adequate answer, samples were prepared made from the various materials that were being considered for the purpose, among others this 14 per cent chromium iron. These were sent to the Gulf Coast, just a few hundred feet from the sea, to get the worst combination of atmosphere and temperature. It was found that the parts made from 14 per cent chromium iron were neither stained nor corroded. That serves to emphasize my point—that it is not possible to set empirical standards for a salt spray test until you have tied it up with your individual requirements.

The importance of this line of reasoning is this:

Many people today are using more expensive types, higher alloy stainless steels than their requirements call for, because they ask for perfection in the salt spray test regardless of whether they actually need that perfection. As a result they pay so many cents a pound more for the material than their requirements would properly call for.

I was interested to notice the authors' evidence that specimens of 14 per cent chromium iron drawn at about 1000 degrees Fahr. showed greater corrosion than when drawn at a higher temperature. This confirms my own experience.

I believe the point of minimum corrosion resistance is coincident with the point of lowest impact values. Both come at a point where the martensite breaks down into its components, and then the physical properties are sliding off at the most rapid rate.

At drawing temperatures below 900 degrees Fahr. the resistance to corrosion is at its maximum value.

Forgetting for the moment the questions of salt spray testing, and considering only service requirements, there are a few comments worth making on the subject of surface preparation—or polishing.

There are in commercial use a number of polishing compounds that have been prepared for polishing other materials, which are not suitable for use in polishing or buffing stainless steel. I refer to compounds that contain iron oxide such as rouge or rust tripoli. From a standpoint of producing the finish they are all right, but they do inoculate the surface of the stainless steel with oxide of iron which causes subsequent rusting.

In watching the authors' lantern slides, one thing interested me particularly. The specimens rusted on the cone almost entirely. The cone is the end grain of the steel. The cylindrical sides represent side grain. It has been my observation that corrosion resisting steels are more likely to show corrosion, if they are going to show it, on the end grain rather than on the side grain. A great deal of corrosion resisting steel is used in the form of plates, sheets, and strips. The end grain is negligible. If the steel is fabricated into stampings or sheet metal parts, the large area that we want to resist corrosion is the flat side of the fiber of the steel. It has been observed many times that if you test the steel in the form of a salt spray specimen, you may reject it on its end grain corrosion, but that same steel rolled out into strip or plate and then formed into a stamping will show very much better corrosion resistance because there the surface represents side grain and not end grain.

As the authors have pointed out, there are so many variables that enter into this matter of salt spray testing that I had fully expected the discussion to be voluminous. All of us have had significant experiences with this test and I thought we would have heard from more than we did. I have suggested just two or three sidelights that I thought might be of interest.

Authors' Closure

Dr. Krivobok has been very kind in his discussion. We think on the whole he agrees pretty much with our observations, and those points which he has brought out show differences mainly in terminology and degree.

Mr. Jones asked a question, and we wish to tell him that length of time between preparation of samples and their exposure, with possible passivation produced by the oxygen of the atmosphere, does not effect the salt spray resistance to an extent that we have been able to observe. The reason may be that the salt spray test is a very severe one, and it has the faculty for breaking down the surface film. Given time it appears to be able to break down a so called "passivated" surface, as for instance one prepared by immersion in warm 20 per cent nitric acid. Nevertheless, this time interval may have an effect which cannot be readily observed due to the impossibility for precise measurement of the effects of the salt spray test.

We appreciate very much what Mr. Palmer has said. Largely, he has supplemented the paper and his remarks require very little comment from us.

He has sized up the salt spray test very carefully. He has found, as we have, that the results of the salt spray test must be mixed with a lot of good judgment, experience and common sense. In this connection, we think it would

not be amiss to emphasize again that the salt spray test is severe. It has no direct parallel in atmospheric corrosion, or in any ordinary corrosion resisting service. Therefore, rusting and staining in the salt spray test do not mean that service conditions will produce similar effects. For one thing, service conditions are not uniform, and there is a good chance for such beneficial influences as we have described in the five 100-hour test to enter.

As for this end grain idea, we left that out of our paper. It is a little different way of putting it than we would have selected. We too have noticed a difference between salt spray resistance of sheet, strip and plate, as compared with bar stock. We do not know that it is so much a matter of end grain as of grain structure. We do feel that there may be something inherent in the processing of strip which makes for better fundamental salt spray resistance than is the case in bar stock. It is true that our corrosion was mainly on the cone surface but it will average up quite largely on the lower parts of the cones. That part of the cone is, of course, closest to the surface of the bar. Thus the end grain at the center, which should be the poorest quality metal, shows less rusting than the end grain at the surface, which should be the best quality end grain.

We checked this possible effect of the end grain in an interesting way. We prepared two specimens out of a 2.5 or 3-inch round bar, and out of a billet, and cut the specimen so that its axis was normal to the axis of rolling. In other words, we cut a specimen out of the bar, and out of the billet so that the cone represented both side and end grain, and the sides of the specimen likewise included both side and end grain. These two specimens rusted on the cones exactly as the specimens shown on the screen.

We wish to thank Dr. Speller for his valued comment. He has counselled caution in applying the salt spray test too broadly, and we echo his counsel. Our paper as presented has been considerably condensed, and we believe Dr. Speller will find that we have given attention to this aspect of the problem in the paper as written.

ON THE NATURE OF THE TETRAGONAL AND CUBIC MARTENSITES

By Kotaro Honda and Zenji Nishiyama

Abstract

This paper deals with the nature of martensite as clarified by means of the X-ray.

Formerly before the crystallographic nature was clearly understood, two theories were held: one, that martensite consisted of a very fine dispersed system, the carbide particles being precipitated in a ferrite groundmass; and two, that martensite consisted of an aggregate of fine crystals of a solid solution of carbon in iron.

Later, however, the X-ray has proved that the first theory is in error and that martensite is in truth a solid solution of carbon in iron, divided into two distinct kinds, alpha in quenched steels and beta in quenched and tempered steels. Definite conclusions are drawn that beta martensite is a solid solution, carbon atoms being present within the space lattice of iron, and it is very probable that in alpha martensite each of the carbon atoms occupies one of the face centers of the tetragonal lattice and in beta martensite a position ($\frac{1}{2}$, $\frac{1}{4}$, 0) of the cubic lattice.

Comparative data are offered contrary to the results set forth by Öhman in the article by Dr. Westgren published recently in METAL PROGRESS to confirm the authors' findings in this respect.

IF a piece of steel is heated above the A_1 point and quenched in water, a structure known as martensite is obtained. The nature of martensite has recently been clarified by several scientists by means of X-ray investigations. It is a solid solution of carbon in iron; the iron atoms in martensite have a body-centered tetragonal lattice, whose a-axis is a little shorter than that of alpha iron and the axial ratio c/a increases from 1.00 to 1.07 as the carbon content increases from 0 to 1.6 per cent. According to views summarized by Dr. A. Westgren[1], the carbon atoms in martensite were thought to occupy positions within the space lattice of iron at points in the (0 0 1) plane, scattered here and there according to the laws of probability.

[1]A. Westgren, "Martensite," *Metal Progress,* August, 1931, p. 49.

About ten years ago, when the essential crystallographic nature of martensite was not well understood, two theories prevailed. The first theory was that martensite consists of a very fine dispersed system, the carbide particles being precipitated in a ferrite groundmass, and that the great hardness is due to the slip interference of the dispersed particles. The second theory was that martensite consists of an aggregate of fine crystals of a solid solution of carbon in iron; in this theory, its great hardness is explained by the combined action of the lattice distortion, internal stress, and the fineness of the crystal grains.

Since then many important investigations have been made, and it has been now proven that the first theory is not valid, but that martensite is in truth a solid solution of carbon in iron. As noted above, one important fact that gave the final decision against the first theory resulted from X-ray investigations; that is, the space lattice of iron atoms in martensite is a body-centered tetragonal lattice, the axial ratio of which increases linearly with the content of carbon. The first part of the above statement (that martensite has a tetragonal lattice) is equally appropriate to either of the two theories above mentioned, but the second portion (that the axial ratio increases with the carbon content) can only be explained by the second theory; for if martensite consists of a mixture of ferrite and carbide as a dispersed system, the axial ratio of the tetragonal lattice must be independent of the carbon content. Hence the conclusion that martensite in a freshly quenched steel has a tetragonal lattice whose parameters depend upon the carbon content.

When such a quenched steel is tempered at about 120 degrees Cent. (250 degrees Fahr.) for 30 minutes or so, the hardness slightly increases, the volume and also the electric resistance decrease, but yet the latter two properties are considerably greater than those of ferrite. Since this tempered substance resembles very much in physical properties the martensite formed on quenching, Dr. T. Matsushita[2] considered it to be another kind of martensite. Thus we have two kinds of martensite, alpha and beta; alpha martensite is found in quenched steels and beta martensite in quenched and tempered steels. It has also been found that the lattice of the iron atoms in the latter is body-centered cubic, as in ferrite.

Many metallurgists consider beta martensite to be a dispersed

[2] T. Matsushita, *Science Reports*, Tohoku Imperial University, Sendai, Japan, Vol. 7, 1918, p. 43.

system consisting of the decomposed product of alpha martensite—that is, a mixture of ferrite and cementite—but the fact that the electric resistance is much greater than that of ferrite indicates that it has characteristics of a solid solution. Its great hardness and the
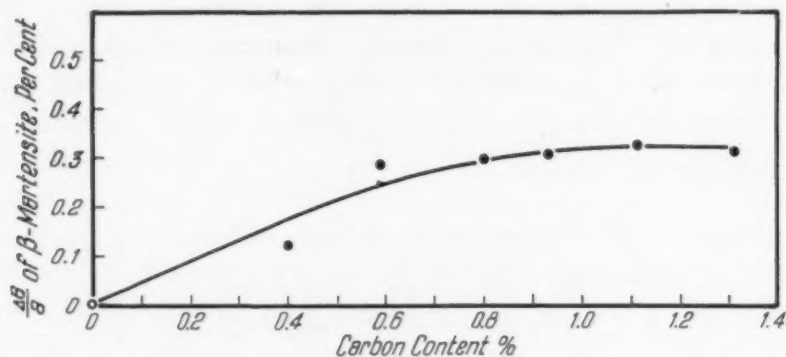

Fig. 1

diffuseness of the X-ray spectral lines also show that the iron lattice is distorted by carbon atoms within it. So the problem of whether beta martensite is a solid solution or a dispersed system, is a very delicate one to decide.

The final decision can, however, be made by measuring the lattice constants and their variation with the carbon content in the martensite, as has been done for alpha martensite. Such an investigation has just been completed with the following result.

Beta martensite has a body-centered cubic lattice, whose lattice constant ($\triangle a \div a$) increases at first linearly and afterwards more slowly, as carbon content increases, the maximum amounting to 0.33 per cent as shown in Fig. 1. The breadth of the spectral lines also increases almost proportionally with the content of carbon (Fig. 2). The reason why the rate of increase of the lattice constant becomes smaller in high carbon steels is explained by the marked broadening of the spectral lines; in this case, the meaning of the mean lattice constant becomes less important.

The above result warrants the decisive conclusion that beta martensite is not a dispersed system consisting of an aggregate of decomposed products (ferrite and cementite) but that it is a solid solution of carbon in iron, the carbon atoms being present within the space lattice of iron.

Since beta martensite is more stable than alpha martensite, the position of the carbon atoms in the lattice should be a more stable one. As we shall show below, it is very probable that in alpha martensite,

each of the carbon atoms occupies one of the face centers of the tetragonal lattice, and in beta martensite a position ($\frac{1}{2}$, $\frac{1}{4}$, 0) of the cubic lattice.

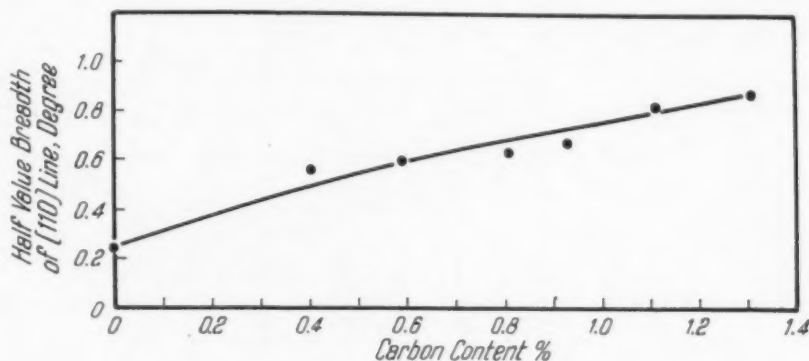About six years ago, one of the present writers[3] showed by

Fig. 2

theoretical considerations that the Ar_1 transformation consists, in its mechanism, of two successive changes; that is,

Gamma iron dissolving carbon → alpha-like iron dissolving carbon → ferrite + cementite. Or, put in other words,

Austenite → martensite → pealite.

At that time martensite was defined as a metastable intermediate product of transformation. Formation of martensite by quenching is satisfactorily explained by the above proposition. The mechanism of the austenite → martensite change was first described by Seljakow, Kurdjumow and Goodtzow[4], but in those days martensite was considered to be body-centered cubic, and hence their explanation requires a little modification to be applicable to the present conception of two kinds of martensites.

Since a face-centered cubic lattice may be regarded as a body-centered tetragonal one with an axial ratio $c/a = \sqrt{2}$ (see Fig. 3) and since a body-centered cubic lattice may also be regarded as a body-centered tetragonal one with an axial ratio $c/a = 1$, the transformation from austenite to martensite may be supposed to take place very probably in the following way:

Tetragonal lattice ($c/a = \sqrt{2}$) → tetragonal lattice ($c/a = 1.03$ to 1.07) → tetragonal lattice ($c/a = 1$). Or, put in other words,

Austenite → alpha martensite → beta martensite.

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[3] *Science Reports*, Tohoku Imperial University, Sendai, Japan, Vol. 14, 1925, p. 165.

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[4] *Zeitschrift fuer Physik*, Vol. 45, 1927, p. 384.

In this view the mechanism of the austenite → martensite change is very simple; it is only necessary that the body-centered tetragonal lattice of austenite should contract in the direction of its c-axis and expand uniformly in perpendicular directions. Alpha martensite is
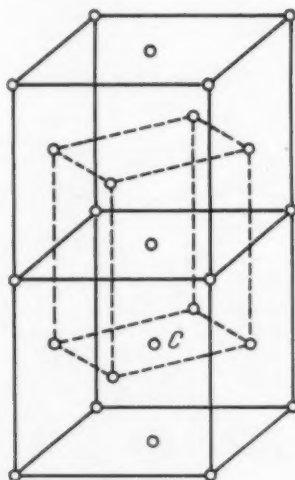

Fig. 3

obtained when the axial ratio of the tetragonal crystal has changed from its original 2 to its value between 1.03 and 1.07, and beta martensite is the end product when the ratio has changed further to 1.

The simplicity of this mechanism explains the question why such a complicated rearrangement of atoms as the change from the face-centered cubic lattice to the body-centered can be correctly performed during a very rapid cooling, such as quenching in water. As one can see in a paper soon to be published in our Science Reports, the result of X-ray investigations made by Y. Kurdjumow and Y. Sachs[5] is not in the least inconsistent with the mechanism above mentioned.

Next we shall consider the position of carbon atoms in the lattice of alpha and beta martensites.

In the austenite lattice, the broadest space is evidently the body-center of the cube. The center of the carbon atom must lie at this point. As we have remarked above, the austenite → martensite change consists of a uniform contraction in the direction of the c-axis and a uniform expansion in the perpendicular directions. During these changes in quenching (which take place at the relatively low temperature of 200 to 300 degrees Cent.) the carbon atoms will probably make little if any change of position relative to the iron

[5]*Zeitschrift fuer Physik*, Vol. 64, 1930, p. 336.

atoms, owing to a very slow diffusion at the low temperature. In this case, as is shown by Seljakow, Kurdjumow and Goodtzow, carbon atoms will assume, after the change, the position of the face-center of the plane (0 0 1) of the body-centered lattice. As is already remarked by Öhman, this position of the carbon atoms is not so stable as the position ($\frac{1}{2}$, $\frac{1}{4}$, 0) in the face of the cube; hence if alpha martensite is tempered at 100 to 150 degrees Cent., the tetragonal lattice is changed into the cubic one, and at the same time the carbon atoms in it will be displaced to the more stable position ($\frac{1}{2}$, $\frac{1}{4}$, 0) resulting in beta martensite. Thus it is to be concluded that in alpha martensite, carbon atoms occupy the face centers of the tetragonal lattice, while in beta martensite, they occupy the position ($\frac{1}{2}$, $\frac{1}{4}$, 0) in the cubic lattice.

Öhman's ideas, quoted with approval by Westgren in *Metal Progress* for August, 1931, do not agree with the above statement. He considers three possibilities, (a) that single carbon atoms are inserted into interstices in the iron lattice of alpha martensite, (b) that single carbon atoms are substituted for iron atoms in the regular lattice positions, and (c) that one iron atom may be replaced by a doublet —two carbon atoms. Öhman concluded that the last supposition was most likely for several reasons, (1) that other di-carbides of metals are known to have a similar tetragonal form, (2) that the lattice may be considered as a simple cube or NaCl structure, where the C_2 groups assume the chlorine positions and stretch the lattice, and (3) that specific gravities calculated from this assumed arrangement correspond to the density of quenched specimens. The following calculations will throw some light on the matter.

Quenched 0.5 per cent carbon steel from 830 degrees Cent. (1525 degrees Fahr.) has very little retained austenite; the principal portion of it consists of alpha martensite. If carbon atoms are in the interstices of the iron lattice, the density of the martensite is given by

$$S = \frac{2 \times \dfrac{55.84}{0.995} \times 1.650 \times 10^{-24}}{2.850^3 \times 1.023 \times 10^{-24}} = 7.82$$

but by the C_2 replacement theory,

$$S = \frac{2 \times 1.650 \times 10^{-24}}{\left(\dfrac{0.995}{55.84} + \dfrac{0.005}{12} \cdot \dfrac{1}{2}\right) \times 2.850^3 \times 1.023 \times 10^{-24}} = 7.72$$

According to Dr. K. Tamaru (Sci. Rep., Vol. 18, 1929, p. 473), the observed value of the density is 7.82, which is in perfect agreement with the value obtained by the interstitial theory.

Again, for a 1.35 per cent carbon steel, quenched from 1065 degrees Cent. (1950 degrees Fahr.) according to the interstitial theory, we have

$$\int = \frac{2 \times \dfrac{55.84}{98.65} \times 1.650 \times 10^{-24}}{2.845^3 \times 1.063 \times 10^{-24}} = 7.63$$

In the C_2 replacement theory,

$$\int = \frac{2 \times 1.650 \times 10^{-24}}{\left(\dfrac{0.9865}{55.84} + \dfrac{0.0135}{12} \cdot \dfrac{1}{2} \right) \times 2.845^3 \times 1.063 \times 10^{-24}} = 7.39$$

The actual observed value by Dr. K. Tamaru is 7.73, which is much nearer to the former value than the latter. Assuming that this specimen contains about 35 per cent of austenite, a plausible assumption, and that the density of austenite is 7.94, we have for the density of the mixture

$$\int = \frac{7.63 \times 65 + 7.94 \times 35}{100} = 7.74$$

which is very near to the observed value.

Thus, contrary to the result obtained by Dr. Öhman, the interstitial theory agrees better with the observed facts, and it would appear that the carbon atoms are within the iron lattice. It also corresponds to the simple mechanism advanced for the transition

Austenite → alpha martensite → beta martensite.

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X-RAY STUDIES OF STEEL WIRES OF MEDIUM CARBON CONTENT

By Norman P. Goss and George L. Clark

Abstract

Results of X-ray studies on steel wires of medium carbon content show in a most striking manner the relationship that exists between X-ray spectra and the physical properties. The X-ray not only gives a splendid picture of the relative grain size but reveals the structure of the matrix in which the particles of Fe_3C are dispersed whether they are in the form of pearlite or sorbite, etc. An accurate knowledge of matrix structure is of the utmost value from a practical point of view. This paper shows how the data concerning grain structure obtained by means of X-ray diffraction methods are related to the physical properties.

IN a recent paper[1] the author made a very interesting statement: "The maximum softness and ductility seem to occur around and probably just below the lower critical temperature 1350 degrees Fahr. up to the point of maximum softness there was no change in the grain size. The changes then must be due to the reactions within the grains themselves which the microscope does not reveal." One of the steel wires used in this investigation had the same analysis as the material used in the paper just referred to, and so the results may be compared. The other steel wire had a much higher carbon content and had much greater variations in the physical properties and X-ray spectra.

Steel No. 1 (0.19 Per Cent Carbon)

A round steel wire containing 0.19 per cent carbon and 0.44 per cent manganese was annealed, and a microscopic examination showed it to be pearlitic. It was given an area reduction of 10 per cent in one draft after which it was again examined micro-

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[1]H. E. Publow, "Notes on the Effect of Various Annealing Temperatures on Cold Worked Low Carbon Steel," *Metals and Alloys*, Vol. 2, No. 1, January, 1931, p. 18.

Of the authors, N. P. Goss a member of the society is metallurgist with the Cold Metal Process Co., of Youngstown, Ohio, and George L. Clark is professor of chemistry, University of Illinois, Urbana, Ill. Manuscript received June 12, 1931.

scopically. The grains were not elongated by this amount of cold work from which it might be inferred that this area reduction did not distort the grains appreciably.

X-ray examination revealed the grains to be completely fragmented with some indications of preferred orientation as shown in Fig. 1. Preferred orientation in general starts to take place only after grain fragmentation is complete. The specimen for X-ray analysis was cut parallel to the wire axis, and the X-ray beam was transmitted at right angles to it. In this kind of fiber structure the grain fragments tend to set the (1 1 0) planes perpendicular to the wire axis and at random about this axis. Orientation takes place by rotation and translation on the (1 1 0) planes which are the slip planes. In any metal or alloy the planes of greatest atomic density and spacing are the slip planes. Regardless of the method of cold working slip always takes place on the slip planes. In alpha iron the (1 1 0) planes are the slip planes, while in copper it is the (1 1 1) planes etc.

An area reduction of only 10 per cent does change the physical properties appreciably as can be seen in the following tabulation in which the physical characteristics of the annealed and cold-worked wires are compared.

Per Cent Area Reduction	Tensile Strength Pounds Per Square Inch	Per Cent Elongation in 2 Inches	Per Cent Area Reduction
Annealed	54,000	46	75
10	74,000	18	62

The greatest change occurs in the elongation which dropped from 46 to 18 per cent. In view of the grain fragmentation that has occurred this is easily accounted for in Fig. 1. This cold-worked wire was cut into short lengths suitable for tensile tests, and annealed at various temperatures between 900 and 1600 degrees Fahr. in 100 degree intervals. All of the heat treated specimens were examined by the microscope and with the X-ray. The structures examined under the microscope were predominately pearlite and some sorbite. Since it is the structure of the ferrite matrix with which we are concerned only the results of X-ray examination along with the physical tests will be considered.

Annealing at 1000 degrees Fahr. did not cause recrystallization and the directional characteristics are still present. In the following tabulation it can be seen that the area reduc-
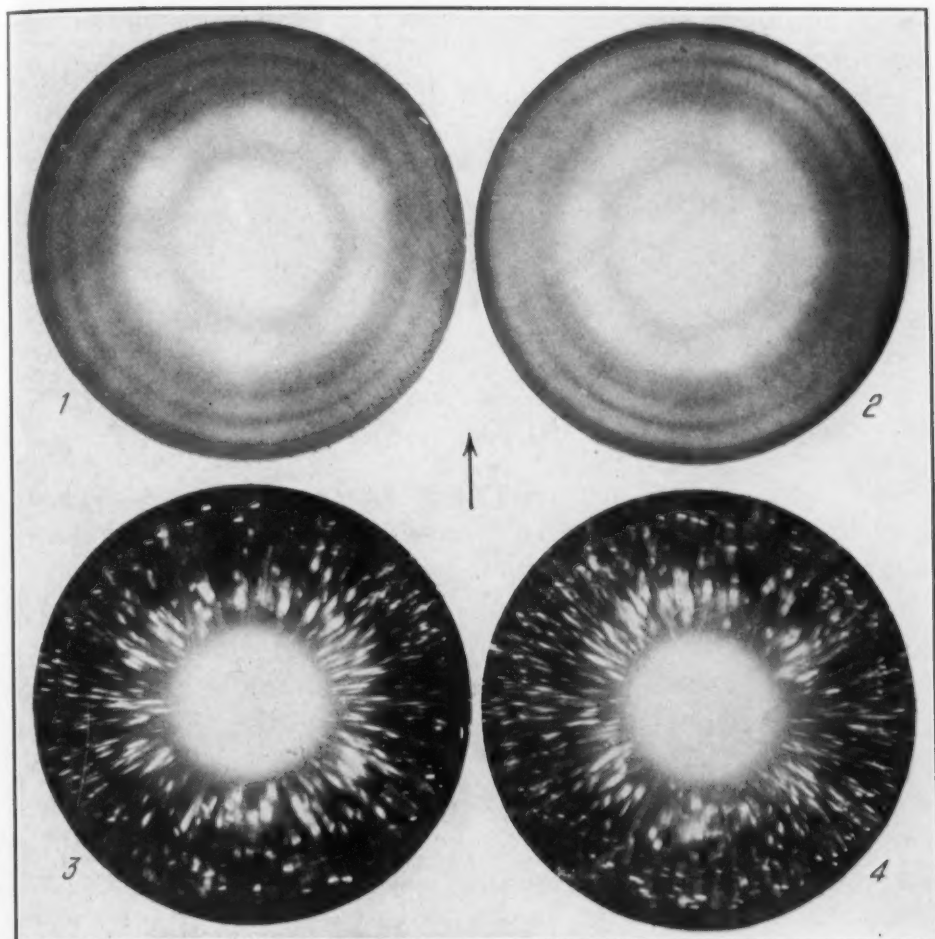
Fig. 1—X-ray Diffraction Pattern of a 0.19 Per Cent Carbon Steel Wire Given an Area Reduction of 10 Per Cent by Drawing Through a Die.

Fig. 2—Diffraction Pattern of a Wire 0.19 per cent Carbon Steel. Wire Given an Area Reduction of 10 Per Cent and Annealed at 1100 Degrees Fahr. for One Hour.

Fig. 3—A Spectrogram of a 0.19 Per Cent Carbon Steel Wire, Reduced 10 per Cent by Drawing and Annealed at 1200 Degrees Fahr.

Fig. 4—X-ray Diffraction Pattern of a 0.19 Per Cent Carbon Steel Wire Annealed at 1300 Degrees Fahr. Arrow Shows Direction of Drawing.

tion has increased appreciably and the tensile strength has been decreased without recrystallization. This can be explained by another method of X-ray crystal analysis which shows that the intensity of the diffraction lines are increased and the K alpha doublet is more sharply resolved. This means that the internal strains have been greatly reduced by this heat treatment.

When annealed at 1100 degrees Fahr. recrystallization of the grain fragments takes place, but it is far from complete as can be seen in Fig. 2. One hour of annealing apparently causes a few grains to

recrystallize, showing that only a few recrystallization nuclei were present at this temperature. This particular wire was annealed for one hour. Other specimens annealed for several hours recrystallized

Annealing Temperature Degrees Fahr.	Tensile Strength Pounds Per Square Inch	Per Cent Elongated in 2 Inches	
As Drafted (10%)	74,000	18	The specimens were
1010	67,000	30	annealed for one
1120	62,000	32	hour at the tem-
1200	55,000	44	peratures indicated
1300	53,000	46	and cooled freely
1400	56,000	37.5	in air.
1500	57,500	37	
1600	59,000	32.5	

in the same way but the grains were larger. Even this slight recrystallization lowered the tensile strength appreciably but the elongation remained the same as shown in the above tabulation.

Annealing at 1200, 1300 and 1400 degrees Fahr. completely recrystallizes the grain fragments produced by cold work. The respective X-ray diffraction patterns are shown in Figs. 3, 4 and 5. The grains appear to be quite large but they are distorted. This distortion was developed during annealing. The physical tests in the above tabulation show that minimum physical properties are developed by annealing at 1300 degrees Fahr. The per cent area reduction is 46 per cent and the tensile strength is 53,000 pounds per square inch. It can also be seen that the tensile strength and the per cent area reduction increased when this wire was annealed at 1400 degrees Fahr., but the X-ray patterns are the same. The increase in this case is explained best by the microstructure which was found to have larger amounts of sorbite present and there was no ferrite at the grain boundaries. The X-ray shows that the structure of the matrix is the same at these annealing temperatures.

When this wire was annealed at 1600 degrees Fahr. for one hour the tensile strength increased to 59,000 pounds per square inch which amounts to an increase of 6000 pounds over the wire annealed at 1300 degrees Fahr. for one hour. Fig. 6 is an X-ray diffraction of this wire. It does not resemble those shown in Figs. 3, 4, and 5 in any respect. The grains are smaller and are slightly fragmented. The increase in tensile strength is accounted for on the basis of smaller grain size and grain fragmentation because the microstructures were similar.

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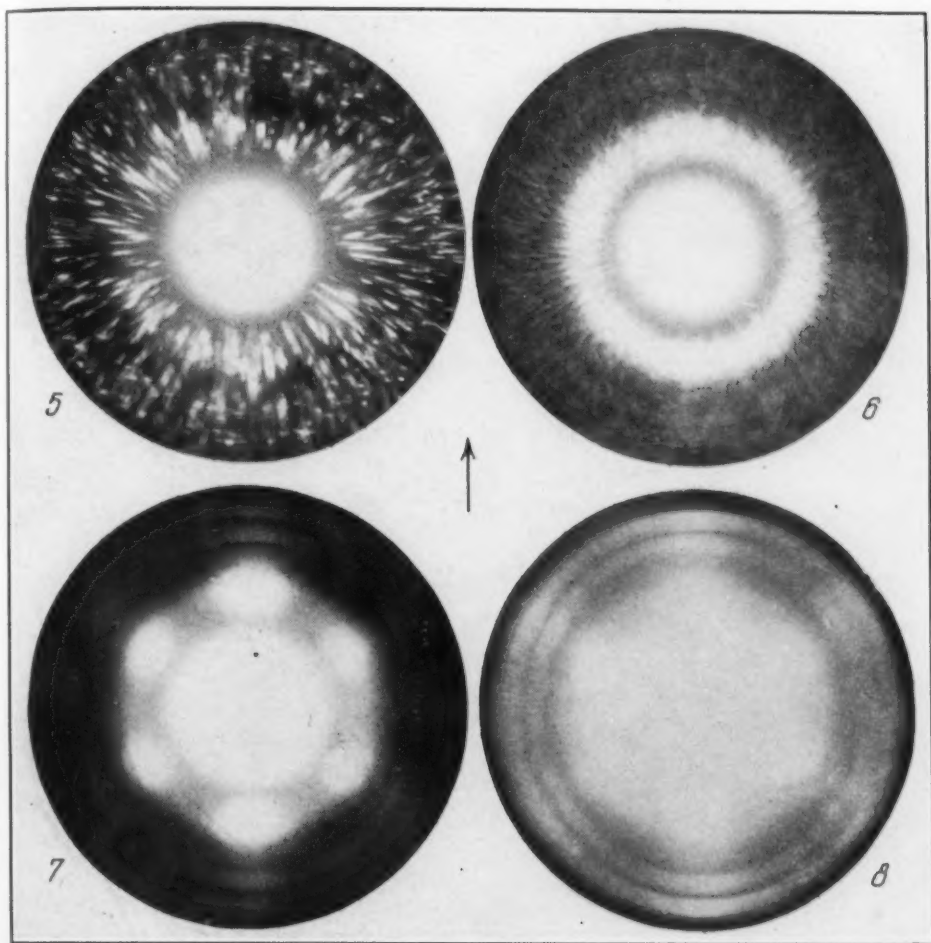nted. The
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Fig. 5—X-ray Diffraction Pattern of a 0.19 Per Cent Carbon Steel Wire Reduced 10 Per Cent by Drawing and Annealed at 1400 Degrees Fahr. for One Hour.
Fig. 6—Spectrogram of a 0.19 Per Cent Carbon Steel Wire Reduced 10 Per Cent by Drawing and Annealed at 1600 Degrees Fahr. for One Hour.
Fig. 7—Spectrogram of a 0.34 Per Cent Carbon Steel Wire Given an Area Reduction of 60 Per Cent.
Fig. 8—Diffraction Pattern of the Same Wire Shown in Fig. 7 After Annealing at 1000 Degrees Fahr. for One Hour. Arrow Shows Direction of Drawing.

Similar tests were made on this wire given greater area reduc-tions. In every case the minimum tensile strength and maximum elongation occurs in wires annealed at 1300 degrees Fahr. and a much greater tensile strength and greatly diminished elongation at 1600 degrees Fahr. The largest grains were always found in the wires annealed at 1300 degrees Fahr. Under proper conditions of draft-ing and annealing grains free of distortion could be developed. Re-gardless of the area reduction prior to annealing at 1600 degrees Fahr. the grains were always found to be small and distorted. This means
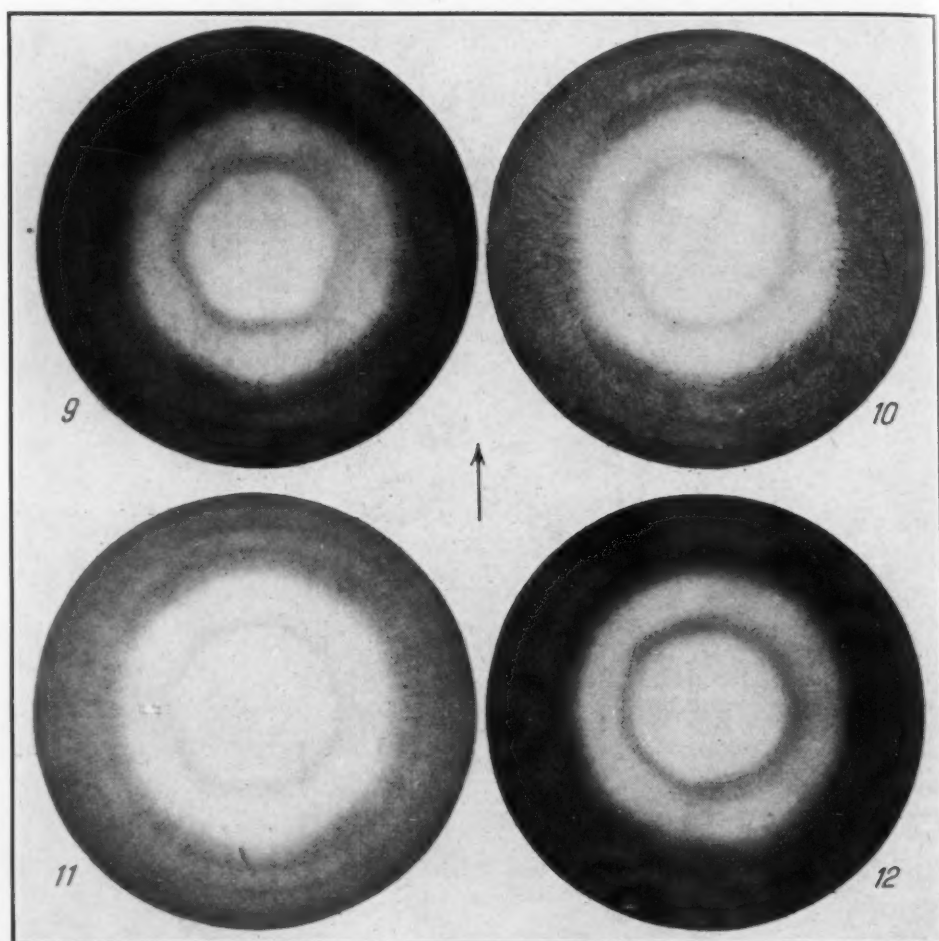
Fig. 9—X-ray Diffraction Pattern of a 0.34 Per Cent Carbon Steel Wire Reduced 60 Per Cent by Drawing and then Annealed at 1200 Degrees Fahr.

Fig. 10—X-Ray Diffraction Pattern of the Same Wire as Fig. 9 but Annealed at 1300 Degrees Fahr.

Fig. 11—X-ray Spectrogram of the Same Wire as Fig. 9 Annealed at 1400 Degrees Fahr. for One Hour.

Fig. 12—X-ray Spectrogram of a 0.34 Per Cent Carbon Steel Wire, Reduced 60 Per Cent by Drawing and Annealed at 1500 Degrees Fahr. for One Hour.   Arrow Shows Direction of Drawing.

that the grain structure can be controlled by annealing at 1300 degrees Fahr.

Regardless of the area reductions when annealed at 1300 degrees Fahr. all had a tensile strength of about 53,000 pounds per square inch but the grain size and structure varied, depending upon the area reduction prior to heat treatment.   Since all the tensile tests were made at rather slow speeds it might be expected that the results would vary in case the rate of loading was increased.

From a crystal structure point of view one can determine by means of the X-ray the proper combination of drawing practice and

heat treatment for producing a matrix structure free of grain distortion or grain size.

STEEL No. 2 (0.34 PER CENT CARBON)

In this part of the investigation a 0.34 per cent carbon steel was studied. The same experimental procedure was used as in the foregoing except that the wire was given a greater area reduction.

The wire was normalized before cold working. It was given an area reduction of 60 per cent by drawing through a wire drawing die. Such a drastic area reduction fibers the wire considerably. Fig. 7 is the X-ray pattern of this wire. It shows that the grains are very small and are oriented with respect to the direction of drafting indicated by the arrow. The [1 1 0] direction tends to coincide with the direction of tension.

Annealing at 1000 degrees Fahr. caused small grains to be recrystallized but it is far from complete as shown in Fig. 8. In spite of the recrystallization the directional characteristics were not removed. This recrystallization modified the physical properties. The tensile strength dropped from 120,000 to 92,000 pounds per square inch and the per cent area reduction increased from 18 to 33 per cent as shown in the following tabulation. Annealing at 1100 degrees Fahr. developed a similar grain structure except that the recrystallization was more complete.

Annealing Temperature Degrees Fahr.	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Per Cent Area Reduction	
		60% Draft		
As Drafted	112,000	120,000	18	
900 .	90,000	114,000	16	All specimens were
1000	68,000	92,000	33	held at the temper-
1100	54,500	73,500	47.5	atures indicated for
1200	47,000	70,500	56	one hour and cooled
1300	38,000	65,500	66	freely in air
1400	41,000	77,500	57	
1500	41,000	80,500	53.5	
1600	43,000	79,000	48	

At 1200 degrees Fahr. recrystallization was complete as shown in Fig. 9. The directional characteristics are still present, which means that the recrystallized grains tend to retain the directional characteristics of the fragmented grains. The tensile strength is again lowered

and the area reduction increased. The X-ray pattern also shows that the grains are not as well developed as they might be.

Annealing at 1300 degrees Fahr. produced the best grain structure. Fig. 10. On comparing it with Fig. 9 the target images are not any larger but are much sharper. This means that these grains
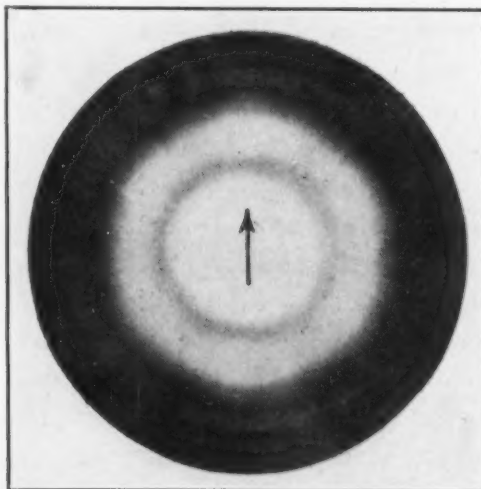

Fig. 13—X-ray Structure of a 0.34 Per Cent Carbon Steel Wire Annealed at 1600 Degrees Fahr. for One Hour. Arrow Shows Direction of Drawing.

are much more perfect in structure. It is interesting to find that the minimum tensile and maximum area reduction and elongation are developed at 1300 degrees Fahr. in the 0.19 per cent carbon and the 0.034 per cent carbon steels.

A great change in grain structure takes place when this wire is annealed at 1400 degrees Fahr. as can be seen in Fig. 11. The grains are not only much smaller but they are distorted. The physical properties also changed in that the tensile increased to 77,500 pounds per square inch, an increase of about 12,000 pounds per square inch, and the per cent area reduction dropped to 57 per cent. The structure was found to be pearlitic-sorbitic under the microscope, quite similar to the structures developed at the other temperatures.

Figs. 12 and 13 show the structures of these wires when heat treated at 1500 and 1600 degrees Fahr. respectively. Grain distortion is more marked in these patterns than in Fig. 11. In fact the grains in the wire heat treated at 1600 degrees Fahr. are distorted the most.

If the preceding tabulation is examined the tensile strengths of

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these three wires are similar but the per cent area reduction was 57 per cent for the wires annealed at 1400 degrees Fahr. and dropped to 48 per cent for the wires annealed at 1600 degrees Fahr.

This means that grain distortion influences the area reduction— the greater the grain distortion the less the area reduction. The greatest area reduction was found in the wires annealed at 1300 degrees Fahr. but here a great many grains were free of distortion.

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